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OF THE
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OF NEW SOUTH WALES

FOR
1943
(INCORPORATED 1881)

VOLUME LXXVII
Parts I-IV

EDITED BY
THE HONORARY SECRETARIES

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CONTENTS

VOLUME LXXVII

Part I *

	Page.
ART. I.—Presidential Address. By H. Priestley, M.D., Ch.M., B.Sc. (Issued November 3, 1943)	1
ART. II.—Nova Puppis 1942. By H. W. Wood. (Issued October 22, 1943) ..	17
ART. III.—A Polyhedral Model of the Projective Plane. By F. A. Behrend. (Issued October 22, 1943)	20
ART. IV.—Preliminary Notes on Solution-Cracking Treatment of Torbanite. By J. A. Dulhanty, B.Sc. (Issued October 22, 1943)	24

Part II †

ART. V.—Tabulata and Heliolitida from the Wellington District, N.S.W. By O. A. Jones, M.Sc. (Communicated by Dr. Ida A. Brown.) (Issued February 9, 1944) ..	33
ART. VI.—The Etch Figures of Basal Sections of Quartz. Their Use in the Orientation of Water-worn Crystals. By F. N. Hanlon, B.Sc., Dip.Ed. (Issued February 9, 1944)	40
ART. VII.—Clarke Memorial Lecture. Australia's Mineral Industry in the Present War. By H. G. Raggatt, D.Sc. (Issued February 9, 1944).. .. .	52

Part III ‡

ART. VIII.—Simple Regression and Correlation. By D. T. Sawkins, M.A. (Issued February 9, 1944)	85
ART. IX.—The Production of Hyoscyamine from Duboisia Species. Part I. Methods of Quantitative Estimation. By J. A. Lean, M.P.S., and C. S. Ralph, B.Sc. (Issued April 17, 1944)	96
ART. X.—The Production of Hyoscyamine from Duboisia Species. Part II. Extraction of the Base. By C. S. Ralph, B.Sc., and J. L. Willis, B.Sc. (Issued April 17, 1944)..	99
ART. XI.—Ebonite as a Radiometer. The Distortion of Ebonite by Long Infra-Red Radiations. By G. G. Blake, F.Inst.P., M.I.E.E. (Issued April 17, 1944).. ..	106
ART. XII.—Studies on Colour Reactions for Sugars. Part I. The Identification and Determination of Monosaccharides with Thymol, Hydrochloric Acid and Ferric Chloride. By A. Bolliger, Ph.D. (Issued April 17, 1944)	109
ART. XIII.—The Chemistry of Bivalent and Trivalent Iridium. Part I. Compounds of Bivalent Iridium Halides with Tertiary Arsines. By F. P. Dwyer, M.Sc., and R. S. Nyholm, M.Sc. (Issued April 17, 1944)	116
ART. XIV.—Stringocephalid Brachiopoda in Eastern Australia. By Ida A. Brown, D.Sc. (Issued April 17, 1944)	119

* Published January 19, 1944.

† Published March 31, 1944.

‡ Published May 16, 1944.

Part IV *

	Page.
ART. XV.—The Vibrations of Square Molecules. Part I. The Normal Coordinates and Vibration Frequencies of Planar AB ₃ Molecules. By Allan Maccoll, M.Sc. (Issued June 23, 1944)	130
ART. XVI.—Further Determinations of Specialisation in Flax Rust Caused by <i>Melampsora Lint</i> (Pers.) Lév. By W. L. Waterhouse, M.Sc., D.Sc.Agr., D.I.C., F.L.S., and I. A. Watson, Ph.D., B.Sc.Agr. (Issued June 23, 1944)	138
ART. XVII.—A Study of the Magnetic Behaviour of Complexes Containing the Platinum Metals. By D. P. Mellor, M.Sc. (Issued June 23, 1944)	145
ART. XVIII.—The Geology of the Cooma District, N.S.W. Part II. The Country between Bunyan and Colinton. By W. R. Browne, D.Sc. (Issued June 23, 1944).. .. .	156
OBITUARY NOTICES	173
TITLE PAGE, CONTENTS, NOTICES, PUBLICATIONS	i
OFFICERS FOR 1943-44	vii
LIST OF MEMBERS, AWARDS OF MEDALS, ETC.	ix
ABSTRACT OF PROCEEDINGS	xxi
PROCEEDINGS OF THE SECTION OF GEOLOGY	xxx
INDEX TO VOLUME LXXVII	xxxiii

NOTICES.

NOTICE.

THE ROYAL SOCIETY of New South Wales originated in 1821 as the "Philosophical Society of Australasia"; after an interval of inactivity, it was resuscitated in 1850, under the name of the "Australasian Philosophical Society", by which title it was known until 1866, when the name was changed to the "Philosophical Society of New South Wales"; in 1866, by the sanction of Her Most Gracious Majesty Queen Victoria, it assumed its present title, and was incorporated by Act of the Parliament of New South Wales in 1881.

TO AUTHORS.

Particulars regarding the preparation of manuscripts of papers for publication in the Society's Journal are to be found in the "Guide to Authors," which is obtainable on application to the Honorary Secretaries of the Society.

FORM OF BEQUEST.

I bequeath the sum of £ to the ROYAL SOCIETY OF NEW SOUTH WALES,
Incorporated by Act of the Parliament of New South Wales in 1881, and I declare that the receipt
of the Treasurer for the time being of the said Corporation shall be an effectual discharge for the
said Bequest, which I direct to be paid within calendar months after my decease,
without any reduction whatsoever, whether on account of Legacy Duty thereon or otherwise,
out of such part of my estate as may be lawfully applied for that purpose.

[Those persons who feel disposed to benefit the Royal Society of New South Wales by Legacies, are recommended to instruct their Solicitors to adopt the above Form of Bequest.]

The following publications of the Society, if in print, can be obtained at the Society's Rooms, Science House, Gloucester and Essex Streets, Sydney.

Transactions of the Philosophical Society, N.S.W., 1862-5, pp. 374, out of print.			
Vols.	I-XI Transactions of the Royal Society, N.S.W., 1867-1877		
Vol.	XII Journal and Proceedings		1878, pp. 324, price 10s. 6d.
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"	XV	"	1881, " 440, "
"	XVI	"	1882, " 327, "
"	XVII	"	1883, " 324, "
"	XVIII	"	1884, " 224, "
"	XIX	"	1885, " 240, "
"	XX	"	1886, " 396, "
"	XXI	"	1887, " 296, "
"	XXII	"	1888, " 390, "
"	XXIII	"	1889, " 534, "
"	XXIV	"	1890, " 290, "
"	XXV	"	1891, " 348, "
"	XXVI	"	1892, " 426, "
"	XXVII	"	1893, " 530, "
"	XXVIII	"	1894, " 368, "
"	XXIX	"	1895, " 600, "
"	XXX	"	1896, " 568, "
"	XXXI	"	1897, " 626, "
"	XXXII	"	1898, " 476, "
"	XXXIII	"	1899, " 400, "
"	XXXIV	"	1900, " 484, "
"	XXXV	"	1901, " 581, "
"	XXXVI	"	1902, " 531, "
"	XXXVII	"	1903, " 663, "
"	XXXVIII	"	1904, " 604, "
"	XXXIX	"	1905, " 274, "
"	XL	"	1906, " 368, "
"	XLI	"	1907, " 377, "
"	XLII	"	1908, " 593, "
"	XLIII	"	1909, " 466, "
"	XLIV	"	1910, " 719, "
"	XLV	"	1911, " 611, "
"	XLVI	"	1912, " 275, "
"	XLVII	"	1913, " 318, "
"	XLVIII	"	1914, " 584, "
"	XLIX	"	1915, " 587, "
"	L	"	1916, " 362, "
"	LI	"	1917, " 786, "
"	LII	"	1918, " 624, "
"	LIII	"	1919, " 414, "
"	LIV	"	1920, " 312, price £1 1s.
"	LV	"	1921, " 418, "
"	LVI	"	1922, " 372, "
"	LVII	"	1923, " 421, "
"	LVIII	"	1924, " 366, "
"	LIX	"	1925, " 468, "
"	LX	"	1926, " 470, "
"	LXI	"	1927, " 492, "
"	LXII	"	1928, " 458, "
"	LXIII	"	1929, " 263, "
"	LXIV	"	1930, " 434, "
"	LXV	"	1931, " 366, "
"	LXVI	"	1932, " 601, "
"	LXVII	"	1933, " 511, "
"	LXVIII	"	1934, " 328, "
"	LXIX	"	1935, " 288, "
"	LXX	"	1936, " 528, "
"	LXXI	"	1937, " 708, "
"	LXXII	"	1938, " 396, "
"	LXXIII	"	1939, " 344, "
"	LXXIV	"	1940, " 658, "
"	LXXV	"	1941, " 224, "
"	LXXVI	"	1942, " 432, "
"	LXXVII	"	1943, " 222, "

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H. H. THORNE, M.A., B.Sc., F.R.A.S.
H. W. WOOD, M.Sc., A.Inst.P., F.R.A.S.

* Died May 11, 1943.

† Elected June 30, 1943.

LIST OF THE MEMBERS
OF THE
Royal Society of New South Wales
as at March 1, 1944

P Members who have contributed papers which have been published in the Society's Journal. The numerals indicate the number of such contributions.

‡ Life Members.

Elected.

1944		Adamson, Colin Lachlan, Chemist, 22 Cremorne-street, Richmond, Vic.
1938	P 2	†Albert, Adrien, Ph.D. <i>Lond.</i> , B.Sc. <i>Syd.</i> , A.I.C. <i>Gt. B.</i> , Commonwealth Research Fellow in Organic Chemistry, University of Sydney; p.r. "Greenknowe," Greenknowe-avenue, Potts Point.
1935		†Albert, Michel Francois, "Boomerang," Billyard-avenue, Elizabeth Bay.
1898		†Alexander, Frank Lee, Surveyor, 67 Ocean-street, Woollahra.
1941		†Alldis, Victor le Roy, L.S., Registered Surveyor, Young, N.S.W.
1905	P 3	†Anderson, Charles, M.A., D.Sc. <i>Edin.</i> , C.M.Z.S., 17 Towns-road, Vacluse. (President, 1924.)
1909	P 12	†Andrews, Ernest C., B.A., Hon. Mem. Washington Academy of Sciences and of Royal Society of New Zealand, No. 4, "Kuring-gai," 241 Old South Head-road, Bondi. (President, 1921.)
1930		Aston, Ronald Leslie, B.Sc., B.E. <i>Syd.</i> , M.Sc., Ph.D. <i>Cantab.</i> , A.M.I.E.E. <i>Aust.</i> , Lecturer in Civil Engineering and Surveying in the University of Sydney; p.r. 24 Redmyre-road, Strathfield.
1919	P 1	Aurousseau, Marcel, B.Sc., 16 Woodland-street, Balgowlah.
1935		Back, Catherine Dorothy Jean, M.Sc., The Women's College, Newtown.
1924	P 1	Bailey, Victor Albert, M.A., D.Phil., F.Inst.P., Professor of Experimental Physics in the University of Sydney.
1934	P 1	Baker, Stanley Charles, M.Sc., A.Inst.P., Head Teacher of Physics, Newcastle Technical College, Tighe's Hill; p.r. 8 Hewison-street, Tighe's Hill, N.S.W.
1937		Baldick, Kenric James, B.Sc., 19 Beaconsfield-parade, Lindfield.
1919		Bardsley, John Ralph, 76 Wright's-road, Drummoyne.
1939	P 2	Basnett, Elizabeth Marie, M.Sc., 36 Cambridge-street, Epping.
1933		Bedwell, Arthur Johnson, Eucalyptus Oil Merchant, "Kama," 10 Darling Point-road, Edgecliff.
1944		Bennett, Alwynne Drysdale, B.Sc., 8 Courland-street, Randwick.
1926		Bentivoglio, Sydney Ernest, B.Sc.Agr., 52 Crows Nest-road, Wollstonecraft.
1940		Betty, Robert Cecil, 67 Imperial-avenue, Bondi.
1937	P 6	Birch, Arthur John, M.Sc., 15 Hilltop-road, Headington, Oxford, England.
1923		Birks, George Frederick, Wholesale Druggist, c/o Potter & Birks Ltd., 15 Grosvenor-street, Sydney; p.r. 42 Powell-street, Killara.
1916		Birrell, Septimus, 74 Edinburgh-road, Marrickville.
1920		Bishop, Eldred George, Manufacturing and General Engineer, 37-45 Myrtle-street, Chippendale; p.r. 17 Thompson-street, Clifton Gardens.
1938		Black, Una Annie Frazer (Mrs.), B.Sc., 16 Melrose, Billyard-avenue, Elizabeth Bay.
1939	P 3	Blake, George Gascoigne, M.I.E.E., F.Inst.P., "Holmleigh," Cecil-avenue, Pennant Hills.
1933	P 22	Bolliger, Adolph, Ph.D., Director of Research, Gordon Craig Urological Research Laboratory, Department of Surgery, University of Sydney.
1920	P 9	Booth, Edgar Harold, M.C., D.Sc., F.Inst.P., New England University College, Armidale. (President, 1935.)
1939	P 1	Bosworth, Richard Charles Leslie, M.Sc., D.Sc. <i>Adel.</i> , Ph.D. <i>Camb.</i> , F.A.C.I., F.Inst.P., c/o C.S.R. Co., Pyrmont; p.r. 41 Spencer-road, Killara.
1938		Breckenridge, Marion, B.Sc., Department of Geology, University of Sydney; p.r. 19 Handley-avenue, Thornleigh.

Elected.

1940		Brigden, Alan Charles, B.Sc., 22 Kelso-street, Enfield.
1919	P 1	Briggs, George Henry, D.Sc., Ph.D., F.Inst.P., Officer-in-Charge, Section of Physics, National Standards Laboratory of Australia, University Grounds, Sydney; p.r. 13 Findlay-avenue, Roseville.
1942		Brown, Desmond J., B.Sc., 9 Agnes-street, Strathfield.
1935	P 4	Brown, Ida Alison, D.Sc., Lecturer in Palaeontology, University of Sydney.
1941		Brown, Samuel Raymond, A.C.A. Aust., 87 Ashley-street, Chatswood.
1913	P 22	Browne, William Rowan, D.Sc., Reader in Geology in the University of Sydney. (President, 1932.)
1940		Buckley, Daphne M. (Mrs.), B.Sc., 4 Sharland-avenue, Chatswood.
1940		Buckley, Lindsay Arthur, B.Sc., 4 Sharland-avenue, Chatswood.
1943		Burfitt, Barbara Joyce, M.B., B.S., Captain, A.I.F., 110 Elizabeth Bay-road, Elizabeth Bay, N.S.W.
1898		†Burfitt, W. Fitzmaurice, B.A., M.B., Ch.M., B.Sc. Syd., F.R.A.C.S., "Radstoke," Elizabeth Bay.
1926		Burkitt, Arthur Neville St. George, M.B., B.Sc., Professor of Anatomy in the University of Sydney.
1943		Burkitt, John Stanton, "Moonbi," 17 Cavell-street, West Hobart, Tas.
1940	P 1	Cane, Reginald Frank, M.Sc., A.A.C.I., National Oil Pty. Ltd., Glen Davis, N.S.W.
1940		Callanan, Victor John, B.Sc., 17 Wheatleigh-street, Naremburn.
1938	P 2	†Carey, Samuel Warren, D.Sc., Practising Petroleum Geologist, c/o Australasian Petroleum Co., Melbourne.
1903	P 5	†Carslaw, Horatio Scott, Sc.D., LL.D., F.R.S.E., Emeritus Professor of Mathematics, University of Sydney, Fellow of Emmanuel College, Cambridge; Burradoo, N.S.W.
1944		Cavill, George William Kenneth, B.Sc., Department of Chemistry, Technical College, Harris-street, Ultimo; p.r. 40 Chandos-street, Ashfield.
1913	P 4	Challinor, Richard Westman, F.I.C., A.A.C.I., A.S.T.C., F.C.S.; p.r. 54 Drumalbyn-road, Bellevue Hill. (President, 1933.)
1933		Chalmers, Robert Oliver, A.S.T.C., Scientific Liaison Bureau, Box 4061, G.P.O., Sydney.
1940		Chambers, Maxwell Clark, B.Sc., c/o J. and E. Atkinson Pty. Ltd., 469-75 Kent-street, Sydney.
1913	P 20	Cheel, Edwin, 40 Queen-street, Ashfield. (President, 1931.)
1935	P 2	Churchward, John Gordon, B.Sc.Agr., Ph.D., 1 Hunter-street, Woolwich.
1935		Clark, Sir Reginald Marcus, K.B.E., Central Square, Sydney.
1940		Clarke, Ronald Stuart, B.A., 28 Becroft-road, Becroft.
1938		Clune, Francis Patrick, Author and Accountant, 15 Prince's-avenue, Vacluse.
1941		Cohen, Max Charles, B.Sc., A.I.F.
1940		Cohen, Samuel Bernard, M.Sc., A.A.C.I., 24 Euroka-street, Northbridge.
1940	P 1	Colditz, Margaret Joyce, B.Sc., 9 Beach-street, Kogarah.
1940		Cole, Edward Ritchie, B.Sc., 14 Barwon-road, Lane Cove.
1940	P 1	Cole, Joyce Marie, B.Sc., 14 Barwon-road, Lane Cove.
1940		Collett, Gordon, B.Sc., 20 Duchess-avenue, Fivedock.
1920		Cooke, Frederick, c/o Meggitt's Limited, Asbestos House, York and Barrack-streets, Sydney.
1913	P 5	Coombs, F. A., F.C.S., Instructor of Leather Dressing and Tanning, Sydney Technical College; p.r. Bannerman-crescent, Rosebery.
1933		Corbett, Robert Lorimer, Managing Director of Robert Corbett & Co. Ltd., Manufacturing Chemists, Head Office, 379 Kent-street, Sydney.
1940		Cortis-Jones, Beverly, M.Sc., 62 William-street, Roseville.
1919		Cotton, Frank Stanley, D.Sc., Research Professor in Physiology in the University of Sydney.
1909	P 7	Cotton, Leo Arthur, M.A., D.Sc., Professor of Geology in the University of Sydney. (President, 1929.)
1941	P 1	Craig, David Parker, Research Scholar, 62 Springdale-road, Killara.
1921	P 1	†Cresswick, John Arthur, A.A.C.I., F.C.S., Production Superintendent and Chief Chemist, c/o The Metropolitan Meat Industry Commissioner, State Abattoir and Meat Works, Homebush Bay; p.r. 101 Villiers-street, Rockdale.
1940	P 4	Crockford, Joan Marian, B.Sc., 219 Victoria-road, Gladesville.
1935	P 3	Culey, Alma Gertrude, M.Sc., 37 Neirbo-avenue, Hurstville.

Elected.

1940		Dadour, Anthony, B.Sc., 25 Elizabeth-street, Waterloo.
1890		Dare, Henry Harvey, M.E., M.Inst.C.E., M.I.E.Aust., 14 Victoria-street, Roseville.
1919	P 2	de Beuzeville, Wilfred Alex. Watt, J.P., "Mélamere," Welham-street, Beecroft.
1906		†Dixson, William, "Merridong," Gordon-road, Killara.
1913	P 3	Doherty, William M., F.I.C., F.A.C.I., 36 George-street, Marrickville.
1928		Donegan, Henry Arthur James, A.S.T.C., A.A.C.I., Analyst, Department of Mines, Sydney; p.r. 18 Hillview-street, Sans Souci.
1943		Dudgeon, William, Manager, Commonwealth Drug Co., 50-54 Kippax-street, Sydney.
1937	P 7	Dulhunty, John Allan, B.Sc., Geology Department, University of Sydney.
1924		Dupain, George Zephirin, A.A.C.I., F.C.S., Director Dupain Institute of Physical Education and Medical Gymnastics, Manning Building, 449 Pitt-street, Sydney; p.r. "Rose Bank," 158 Parramatta-road, Ashfield.
1934	P 20	Dwyer, Francis P. J., M.Sc., Lecturer in Chemistry, Technical College, Sydney.
1923	P 21	Earl, John Campbell, D.Sc., Ph.D., Professor of Organic Chemistry in the University of Sydney. (President, 1938.)
1924		Eastaugh, Frederick Alldis, A.R.S.M., F.I.C., Professor in Engineering Technology and Metallurgy in the University of Sydney.
1934	P 2	Elkin, Adolphus Peter, M.A., Ph.D., Professor of Anthropology in the University of Sydney. (President, 1940. Hon. Secretary.)
1940		Emmerton, Henry James, B.Sc., 41 Nelson-street, Gordon.
1937		English, James Roland, L.S. A.I.F.
1916	P 2	Enright, Walter John, B.A., Solicitor, High-street, West Maitland; p.r. Regent-street, West Maitland.
1908		†Esdaile, Edward William, 42 Hunter-street, Sydney.
1935		Evans, Silvanus Gladstone, A.I.A.A. Lond., A.R.A.I.A., 6 Major-street, Coogee.
1939		Faull, Norman Augustus, B.Sc., A.Inst.P., c/o National Standards Laboratory, University Grounds, City-road, Chippendale.
1909	P 7	†Fawsitt, Charles Edward, D.Sc., Ph.D., Professor of Chemistry in the University of Sydney. (President, 1919.)
1923		Fiaschi, Piero, O.B.E., V.D., M.D. <i>Columbia Univ.</i> , D.D.S. <i>New York</i> , M.R.C.S. <i>Eng.</i> , L.R.C.P. <i>Lond.</i> , 178 Phillip-street, Sydney.
1940		Finch, Arthur Charles Allenby, B.Sc., Kirby-street, Rydalmere, N.S.W.
1927	P 7	Finnemore, Horace, B.Sc., F.I.C., Reader in Pharmacy in the University of Sydney.
1940		Fisher, Robert, B.Sc., 3 Sackville-street, Maroubra.
1920		Fisk, Sir Ernest Thomas, K.B., F.Inst.R.E., A.M.I.E. <i>Aust.</i> , Chairman of Directors, Amalgamated Wireless (Australasia) Ltd., Wireless House, 47 York-street, Sydney; p.r. 16 Beaconsfield-parade, Lindfield.
1940		Flack, Arthur Charles Allenby, B.Sc., Agricultural High School, Yanco, N.S.W.
1933		Fletcher, Harold Oswald, Assistant Palaeontologist, Australian Museum, College-street, Sydney.
1879		†Foreman, Joseph, M.R.C.S. <i>Eng.</i> , L.R.C.P. <i>Edin.</i> , "The Astor," Macquarie-street, Sydney.
1932		Forman, Kenn. P., M.I.Refr.E., c/o Department of Aircraft Production, Box 20935, Melbourne, Vic.
1905		†Foy, Mark, c/o Geo. O. Bennett, 133 Pitt-street, Sydney.
1940		Franki, Robert James Anning, B.Sc., 891 New South Head-road, Rose Bay.
1943		Frederick, Robert Desider Louis, B.E., 6 "Trinity Court," Telopea-street, Wollstonecraft.
1940		Freney, Martin Raphael, B.Sc., Central Wool Testing House, 17 Randle-street, Sydney.
1935	P 2	Garretty, Michael Duhan, M.Sc., Chief Geologist, North Broken Hill Ltd., Broken Hill, N.S.W.
1939	P 2	Gascoigne, Robert Mortimer, 5 Werona-avenue, Killara.
1926		Gibson, Alexander James, M.E., M.Inst.C.E., M.I.E.Aust., Consulting Engineer, 906 Culwulla Chambers, 67 Castlereagh-street, Sydney; p.r. "Wirruna," Belmore-avenue, Wollstonecraft.
1942		Gibson, Neville Allan, B.Sc., Industrial Chemist, 217 Parramatta-road, Haberfield.
1940		Gillis, Richard Galvin, 1 Dundee, 35 Adams-street, South Yarra, S.E.1, Vic.
1935		Goddard, Roy Hamilton, F.C.A. <i>Aust.</i> , Royal Exchange, Bridge-street, Sydney.

Elected.

- 1936 Goulston, Edna Maude, B.Sc., Third Officer, W.R.A.N.S., Navy Office, Melbourne.
- 1940 Graves, John Nevil, B.Sc., 96 Wentworth-street, Randwick.
- 1938 Griffiths, Edward L., B.Sc., A.A.C.I., A.I.C., Chief Chemist, Department of Agriculture; p.r. 151 Wollongong-road, Arncliffe.
- 1934 Hall, Norman Frederick Blake, M.Sc., Chemist, Council for Scientific and Industrial Research (Tobacco Section), Dept. of Organic Chemistry, University of Sydney; p.r. 15A Wharf-road, Longueville.
- 1992 †Holloran, Henry Ferdinand, L.S., A.M.I.E.Aust., F.S.I.Eng., M.T.P.I.Eng., 153 Elizabeth-street, Sydney; p.r. 23 March-street, Bellevue Hill.
- 1940 P 1 Hanlon, Frederick Noel, B.Sc., Geologist, Department of Mines, Sydney; p.r. 14 Countess-street, Mosman.
- 1905 P 6 †Harker, George, D.Sc., F.A.C.I.; p.r. 89 Homebush-road, Strathfield.
- 1936 Harper, Arthur Frederick Alan, M.Sc., A.Inst.P., National Standards Laboratory, University Grounds, City-road, Chippendale.
- 1934 Harrington, Herbert Richard, Teacher of Physics and Electrical Engineering, Technical College, Harris-street, Ultimo.
- 1929 Hawley, J. William, J.P., Financial Agent, 4 Castlereagh-street, Sydney; p.r. 12 King's-road, Vaucluse.
- 1934 Hayes, William Lyall, A.S.T.C., A.A.C.I., Works Chemist, c/o Messrs. Wm. Cooper & Nephews (Aust.) Ltd., Phillip-street, Concord; p.r. 101 Essex-street, Epping.
- 1919 Henriques, Frederick Lester, 208 Clarence-street, Sydney.
- 1938 P 4 Hill, Dorothy, M.Sc. Q'ld., Ph.D. *Cantab.*, Geological Research Fellow, University of Queensland, Brisbane.
- 1918 Hindmarsh, Percival, M.A. B.Sc.Agr., Principal, Hurlstone Agricultural High School, Glenfield.
- 1936 Hirst, Edward Eugene, A.M.I.E., Vice-Chairman and Joint Managing Director, British General Electric Co. Ltd.; p.r. "Springmead," Ingleburn.
- 1928 Hirst, George Walter Cansdell, B.Sc., A.M.I.E. (Aust.), A.M.Inst.T.; p.r. "St. Cloud," Beaconsfield-road, Chatswood.
- 1916 Hoggan, Henry James, A.M.I.M.E. Lond., A.M.I.E. Aust., Consulting and Designing Engineer, "Lincluden," 81 Frederick-street, Rockdale.
- 1941 Howard, Harold Theodore Clyde, B.Sc., Principal, Wollongong Technical High School, Wollongong.
- 1935 Howarth, Mark, F.R.A.S., Grange Mount Observatory, Bull-street, Mayfield, Newcastle, N.S.W.
- 1938 P 4 Hughes, Gordon Kingsley, B.Sc., Lecturer in Chemistry, University of Sydney.
- 1923 P 3 †Hynes, Harold John, D.Sc., B.Sc.Agr., Biologist, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. "Belbooree," 10 Wandella-avenue, Roseville.
- 1943 Iredale, Thomas, B.Sc., D.Sc., F.I.C., Chemistry Department, University of Sydney; p.r. 96 Roseville-avenue, Roseville.
- 1940 Jaeger, John Conrad, M.A., D.Sc., c/o Radiophysics Laboratory, The University, Sydney.
- 1942 P 1 Johns, Thomas Harley, 130 Smith-street, Summer Hill.
- 1940 Johnston, Thomas Harvey, M.A., D.Sc., C.M.Z.S., Professor of Zoology in the University of Adelaide. (Cor. Mem., 1912.)
- 1909 P 15 Joplin, Germaine Anne, B.Sc., Ph.D., Geological Department, University of Sydney; p.r. 18 Wentworth-street, Eastwood.
- 1935 P 6 Judd, William Percy, 123 Wollongong-road, Arncliffe.
- 1930 Julius, Sir George A., Kt., B.Sc., B.E., M.I.Mech.E., M.I.E.Aust., Culwulla Chambers, Castlereagh-street, Sydney.
- 1911 Kelly, Caroline Tennant (Mrs.), "Eight Bells," Castle Hill.
- 1935 Kennard, William Walter, 9 Bona Vista-avenue, Maroubra.
- 1940 P 1 Kenny, Edward Joseph, Geological Surveyor, Department of Mines, Sydney; p.r. 17 Alma-street, Ashfield.
- 1924 Kerslake, Richmond, A.S.T.C., A.A.C.I., Industrial Chemist, c/o Australian Paper Mfrs. Ltd., Macauley-street, Matraville; p.r. 55 Harold-street, Matraville.

Elected.

1943		Kimble, Jean Annie, Research Chemist, B.Sc., 383 Marrickville-road, Marrickville.
1940		King, Leonard Esmond, 161 Nelson Bay-road, Bronte.
1920		Kirchner, William John, B.Sc., A.A.C.I., Manufacturing Chemist, c/o Messrs. Burroughs Wellcome & Co. (Australia) Ltd., Victoria-street, Waterloo: p.r. 18 Lyne-road, Cheltenham.
1939		Lambeth, Arthur James, B.Sc., "Naranje," Sweethaven-road, Wetherill Park, N.S.W.
1936		Leach, Stephen Laurence, B.A., B.Sc., A.A.C.I., P.O. Box. No. 21, Concord.
1936	P 3	Lemberg, Max Rudolf, D.Phil., Biochemist, Royal North Shore Hospital; p.r. 12 de Villiers-avenue, Chatswood.
1920		Le Souef, Albert Sherbourne, 3 Silex-road, Mosman.
1929	P 55	†Lions, Francis, B.Sc., Ph.D., A.I.C., Department of Chemistry, University of Sydney.
1942		Lippmann, Arthur S., M.D., 175 Macquarie-street, Sydney.
1940	P 1	Lipson, Menzie, B.Sc., Chemist, C.S.I.R., Central Wool Committee Testing House, 17 Randle-street, Sydney.
1940	P 1	Lockwood, William Hutton, B.Sc., c.o. Department of Post-War Reconstruction, Hotel Acton, Canberra, A.C.T.
1906		†Loney, Charles Augustus Luxton, M.Am.Soc.Refr.E., National Mutual Building, 350 George-street, Sydney.
1927	P 1	Love, William Henry, B.Sc., Ph.D., Lecturer in Physics, University of Sydney.
1943		Luber (Mrs.) Daphne, B.Sc., 98 Lang-road, Centennial Park.
1940		Luciano, Albert Anthony, 16 Arthur-street, Bellevue Hill.
1942		Lyons, Raymond Norman Matthew, M.Sc., Biochemical Research Worker, 8 Boronia-avenue, Wollstonecraft.
1939	P 2	Maccoll, Allan, M.Sc., 76 Springdale-road, Killara.
1943		McCoy, William Kevin, Analytical Chemist.
1940		McGrath, Brian James, 40 Mooramie-avenue, Kensington.
1940		McGregor, Gordon Howard, 4 Maple-avenue, Pennant Hills.
1906	P 2	†McIntosh, Arthur Marshall, "Moy Lodge," Hill-street, Roseville.
1891	P 1	†McKay, R. T., M.Inst.C.E., Eldon Chambers, 92 Pitt-street, Sydney.
1943		McKern, Howard Hamlet Gordon, A.S.T.C., A.A.C.I., Chemist, Meggitt Ltd., Parramatta; p.r. 14 Orwell-street, Potts Point.
1932		McKie, Rev. Ernest Norman, B.A. Syd., St. Columba's Manse, Guyra.
1927		McMaster, Sir Frederick Duncan, Kt., "Dalkeith," Cassilis, N.S.W.
1940		Malone, Edward E., No. 4, Astral, 10 Albert-street, Randwick.
1924		Mance, Frederick Stapleton, "Binbah," Lucretia-avenue, Longueville.
1944		Martin, Cyril Maxwell, Chemist, 22 Wattle-street, Haberfield.
1935		Maze, Wilson Harold, M.Sc., Lecturer in Geography, University of Sydney.
1941		Melville, George Livingstone, Managing Director, Federal Machine Co. Ltd., Loftus-street, Arncliffe.
1912		Meldrum, Henry John, B.A., B.Sc., Lecturer, The Teachers' College, University Grounds, Newtown; p.r. 98 Sydney-road, Manly.
1929	P 19	Mellor, David Paver, M.Sc., Lecturer, Chemistry Department, University of Sydney; p.r. 137 Middle Harbour-road, Lindfield. (President, 1941-42. Joint Hon. Secretary.)
1940		Mercer, Edgar Howard, McMaster Laboratory, Parramatta-road, Glebe.
1928		Micheli, Louis Ivan Allan, M.Sc., Ph.D., Research Chemist, c/o Colonial Sugar Refining Co., Pyrmont.
1940		Millership, William, M.Sc., Chief Chemist, Davis Gelatine (Aust.) Pty. Ltd., 15 Shaw-avenue, Earlwood.
1943		Molloy, Ernest Patrick, Assistant Sectional Manager, 129 Gibbes-street, Rockdale.
1941		Morrissey, Matthew John, B.A., A.S.T.C., Auburn-street, Parramatta.
1922	P 27	Morrison, Frank Richard, A.A.C.I., F.C.S., Assistant Chemist, Technological Museum, Sydney.
1934		Mort, Francis George Arnot, A.A.C.I., Chemist, 16 Grafton-street, Woollahra.
1944		Moye, Daniel George, Chemist, 89 Caroline-street, South Yarra, S.E.1., Vic.

Elected.

1915		Murphy, Robert Kenneth, Dr.ing., Chem.Eng., A.S.T.C., M.I.Chem.E., A.A.C.I., Lecturer in Charge of Chemistry and Head of Science Department, Sydney Technical College.
1923	P 2	Murray, Jack Keith, QX34748, B.A., B.Sc.Agr., N.E. Reinf. Training Centre, Warwick, Queensland, and Professor of Agriculture in the University of Queensland.
1930	P 6	Naylor, George Francis King, M.A., M.Sc., Dip.Ed., A.A.I.I.P., Squadron Leader, R.A.A.F., Headquarters, Melbourne; p.r. "Kingsleigh," Ingleburn, N.S.W.
1943		Neuhaus, John William George, c/o Meggitt and Co. Ltd., Parramatta.
1932		Newman, Ivor Vickery, M.Sc., Ph.D., F.R.M.S., F.L.S., Department of Biology, Victoria University College, Wellington, N.Z.
1943		Nicol, Alexander Campbell, A.S.T.C., A.A.C.I., Chief Chemist, Crown Crystal Glass Co.; p.r. No. 12 "Florida," 519 New South Head-road, Double Bay.
1920	P 4	†Noble, Robert Jackson, M.Sc., B.Sc.Agr., Ph.D., Under Secretary, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. 32A Middle Harbour-road, Lindfield. (President, 1934.)
1940		Norrie, Jack Campbell, B.Sc., 28 Ray-road, Epping.
1940	P 7	Nyholm, Ronald Sydney, M.Sc., 77 Bland-street, Ashfield.
1935		O'Connell, Rev. Daniel J. K., S.J., M.Sc., F.R.A.S., Riverview College Observatory, Sydney.
1903		†Old, Richard, "Waverton," Bay-road, North Sydney.
1921	P 5	Osborne, George Davenport, D.Sc. <i>Syd.</i> , Ph.D. <i>Camb.</i> , Lecturer and Demonstrator in Geology in the University of Sydney.
1920	P 74	Penfold, Arthur Ramon, F.A.C.I., F.C.S., Curator and Economic Chemist, Technological Museum, Harris-street, Ultimo; p.r. 67 Park-avenue, Roseville. (President, 1935.)
1940		Pettingell, William Walter, B.Sc., 28 Conder-street, Burwood.
1938		Phillips, Marie Elizabeth, B.Sc., 4 Morella-road, Clifton Gardens.
1935		Phillips, Orwell, 55 Darling Point-road, Edgecliffe.
1943		Plowman, Ronald Arthur, A.S.T.C., A.A.C.I., Analytical Chemist, 78 Alt-street, Ashfield.
1919		Poate, Hugh Raymond Guy, M.B., Ch.M. <i>Syd.</i> , F.R.C.S. <i>Eng.</i> , L.R.C.P. <i>Lond.</i> , F.R.A.C.S., Surgeon, 225 Macquarie-street, Sydney; p.r. 38 Victoria-road, Bellevue Hill.
1896		†Pope, Roland James, B.A. <i>Syd.</i> , M.D., Ch.M., F.R.C.S. <i>Edin.</i> , 185 Macquarie-street, Sydney.
1921	P 2	Powell, Charles Wilfrid Roberts, F.I.C., A.A.C.I., Company Executive, c/o Colonial Sugar Refining Co., O'Connell-street, Sydney; p.r. "Wansfell," Kirkoswald-avenue, Mosman.
1918		Powell, John, Director, Foster Clark (Aust.) Ltd., 17 Thurlow-street, Redfern; p.r. "Elgarth," Ranger's-road, Cremorne.
1938		Powell, John Wallis, A.S.T.C., A.A.C.I., Managing Director, Foster Clark (Aust.) Ltd., 17 Thurlow-street, Redfern.
1927		Price, William Lindsay, B.E., B.Sc., Teacher of Physics, Sydney Technical College; p.r. 8 Wattle-street, Killara.
1918	P 1	Priestley, Henry, M.D., Ch.M., B.Sc., Professor of Biochemistry, Faculty of Medicine, the University of Sydney. (President, 1942-43.)
1893		†Purser, Cecil, B.A., M.B., Ch.M. <i>Syd.</i> , "Ascot," Grosvenor-road, Wahroonga.
1935	P 3	†Quodling, Florrie Mabel, B.Sc., Demonstrator in Geology, University of Sydney.
1922	P 6	Raggatt, Harold George, D.Sc., Director, Mineral Resources Survey, Department of Supply, Canberra, A.C.T.
1940	P 1	Ralph, Colin Sydney, B.Sc., 24 Canberra-street, Epping.
1919	P 3	Ranclaud, Archibald Boscawen Boyd, B.Sc., B.E., Lecturer in Physics, Teachers' College, The University, Sydney.

Elected.

1936		Randall, Harry, Buena Vista-avenue, Denistone.
1931	P 1	Rayner, Jack Maxwell, B.sc., F.mst.P., Chief Geophysicist, Mineral Resources Survey, Department of Supply and Shipping, Census Building, Canberra, A.C.T.
1935		Reid, Cicero Augustus, 19 Newton-road, Strathfield.
1939	P 6	Ritchie, Ernest, B.sc., 6 Military-road, North Bondi.
1933		Roberts, Richard George Crafter, Electrical Engineer, c/o C. W. Stirling & Co., Asbestos House, York and Barrack-streets, Sydney.
1940		Robertson, Rutherford Ness, B.sc. <i>Syd.</i> , Ph.D. <i>Cantab.</i> , Flat 4, 43 Johnston-street, Annandale.
1935	P 2	Room, Thomas G., M.A., F.R.S., Professor of Mathematics in the University of Sydney.
1940		Rosenbaum, Sidney, 44 Gilderthorp-avenue, Randwick.
1928		Ross, Allan Clunies, B.sc., F.C.A. <i>Aust.</i> , Chartered Accountant <i>Aust.</i> , 54A Pitt-street, Sydney; p.r. The Grove, Woollahra. (Member from 1915 to 1924.) (Hon. Treasurer.)
1940		Ross, Jean Elizabeth, B.sc., Dip.Ed., 5 Stanton-road, Haberfield.
1935		Savage, Clarence Golding, Director of Fruit Culture, Department of Agriculture, Sydney.
1941	P 2	Sawkins, Dansie Thomas, M.A. <i>Syd.</i> , B.A. <i>Camb.</i> , Reader in Statistics, The University, Sydney; p.r. 60 Boundary-street, Roseville.
1920		Scammell, Rupert Boswood, B.sc. <i>Syd.</i> , A.A.C.I., F.C.S., c/o F. H. Faulding & Co. Ltd., 98 Castlereagh-street, Redfern; p.r. 10 Buena Vista-avenue, Clifton Gardens.
1940		Scott, Reginald Henry, B.sc., 154 Highfield-road, Camberwell, Vic.
1933		Selby, Esmond Jacob, Dip.Com., Sales Manager, Box 175 D, G.P.O., Sydney.
1936		Sellenger, Brother Albertus, Marist Brothers' College, Randwick, N.S.W.
1938		Sheahan, Thomas Henry Kennedy, B.sc., Chemist, 2 Edward-street, Gordon.
1936	P 2	Sherrard, Kathleen Margaret Maria (Mrs.), M.sc. <i>Melb.</i> , 43 Robertson-road, Centennial Park.
1917		Sibley, Samuel Edward, Mount-street, Coogee.
1900		†Simpson, R. C., Lecturer in Electrical Engineering, Technical College, Sydney.
1943		Simpson, John Kenneth Moore, Industrial Chemist, "Browie," Old Castle Hill-road, Castle Hill.
1933		Slade, George Hermon, B.sc., Director, W. Hermon Slade & Co. Ltd., Manufacturing Chemists, 23 Rosebery-avenue, Rosebery; p.r. "Raiaeta," Oyama-avenue, Manly.
1940		Smith, Eric Brian Jeffcoat, 1 Rocklands-road, Wollstonecraft.
1922	P 1	Smith, Thomas Hodge, Australian Museum, College-street, Sydney.
1919		Southee, Ethelbert Ambrook, O.B.E., M.A., B.sc., B.sc.Agr., Principal, Hawkesbury Agricultural College, Richmond, N.S.W.
1921		Spencer-Watts, Arthur, "Araboonoo," Glebe-street, Randwick.
1916		Stephen, Alfred Ernest, F.C.S., c/o Box 1158 HH, G.P.O., Sydney.
1914		Stephens, Frederick G. N., F.R.C.S., M.B., Ch.M., 135 Macquarie-street, Sydney; p.r. Captain Piper's-road and New South Head-road, Vaucluse.
1900	P 1	†Stewart, J. Douglas, B.v.sc., F.R.C.v.s., Emeritus Professor of Veterinary Science in the University of Sydney; p.r. "Berelle," Homebush-road, Strathfield. (President, 1927.)
1942		Still, Jack Leslie, B.sc., Ph.D., Department of Biochemistry, The University, Sydney.
1909		†Stokes, Edward Sutherland, M.B., Ch.M. <i>Syd.</i> , D.P.H. <i>Irel.</i> , Medical Officer, Metropolitan Board of Water Supply and Sewerage, 341 Pitt-street, Sydney; p.r. 15 Highfield-road, Lindfield.
1916	P 1	Stone, Walter George, F.S.T.C., A.A.C.I., Senior Analyst, Department of Mines, Sydney; p.r. 14 Rivers-street, Bellevue Hill.
1940		Stroud, Richard Harris, B.sc., "Dalveen," corner Chalmers and Barker-roads, Strathfield.
1918		†Sullivan, Herbert Jay, Director in Charge of Research and Technical Department, c/o Lewis Berger & Sons (Australia) Ltd., Rhodes; Box 23, P.O., Burwood; p.r. "Stonycroft," 10 Redmyre-road, Strathfield.
1901	P 16	†Sussemilch, C. A., F.G.S., F.S.T.C., Consulting Geologist, 11 Appian Way, Burwood. (President, 1922.)
1919		†Sutherland, George Fife, A.R.C.sc. <i>Lond.</i> , Assistant Professor of Mechanical Engineering in the University of Sydney.

Elected.

1920		Sutton, Harvey, O.B.E., M.D., D.F.H. <i>Melb.</i> , B.Sc. <i>Oxon.</i> , Professor of Preventive Medicine and Director, School of Public Health and Tropical Medicine, University of Sydney; p.r. "Lynton," 27 Kent-road, Rose Bay.
1941	P 2	Swanson, Thomas Baikie, M.Sc. <i>Adel.</i> , Lecturer in Chemistry, New England University College, Armidale.
1915	P 3	Taylor, Brigadier Harold B., M.C., D.Sc., F.I.C., F.A.C.I., Second Government Analyst, Department of Public Health, 93 Macquarie-street, Sydney; p.r. 44 Kenneth-street, Longueville.
1944		Thomas, Andrew David, Flight-Lieutenant, R.A.A.S., M.Sc., A.Inst.P., 1 Valley-road, Lindfield.
1939		Thomas, Mrs. A. V. M., 1 Valley-road, Lindfield.
1919		Thorne, Harold Henry, M.A. <i>Cantab.</i> , B.Sc. <i>Syd.</i> , F.R.A.S., Lecturer in Mathematics in the University of Sydney; p.r. 55 Railway-crescent, Beecroft.
1935		Tommerup, Eric Christian, M.Sc., A.A.C.I.
1923		Toppin, Richmond Douglas, A.I.C., 51 Crystal-street, Petersham.
1940		Tow, Aubrey James, M.Sc., No. 5, "Werrington," Manion-avenue, Rose Bay.
1932	P 8	Trikojus, Victor Martin, B.Sc., D.Phil., Professor of Biochemistry, The University, Melbourne.
1943		Turner, Ivan Stewart, M.A., M.Sc., Ph.D., Lecturer in Mathematics, University of Sydney; p.r. 120 Awaba-street, Mosman.
1940		Vernon, James, Ph.D., A.A.C.I., Chief Chemist, Colonial Sugar Refining Co., 1 O'Connell-street, Sydney.
1921		Vicars, Robert, Marrickville Woollen Mills, Marrickville.
1935		Vickery, Joyce Winifred, M.Sc., Botanic Gardens, Sydney; p.r. 17 The Promenade, Cheltenham.
1933	P 5	Voisey, Alan Heywood, M.Sc., Lecturer in Geology and Geography, New England University College, Armidale.
1903	P 9	†Vonwiller, Oscar U., B.Sc., F.Inst.P., Professor of Physics in the University of Sydney. (President, 1930.)
1943		Walker, James Foote, Company Secretary, 11 Bruce-avenue, Epping.
1919	P 1	Walkom, Arthur Bache, D.Sc., Director, Australian Museum, Sydney; p.r. 45 Nelson-road, Killara. (Member from 1910-1913. President, 1943-44.)
1913	P 5	Wardlaw, Hy. Sloane Halcro, D.Sc. <i>Syd.</i> , F.A.C.I., Lecturer and Demonstrator in Biochemistry in the University of Sydney. (President, 1939.)
1921		†Waterhouse, Gustavus Athol, D.Sc., B.E., F.R.E.S., F.R.Z.S., c.o. Australian Museum, College-street, Sydney.
1924		Waterhouse, Leslie Vickery, B.E. <i>Syd.</i> , Mining Engineer, Shell House, Carrington-street, Box 58 CC, G.P.O., Sydney; p.r. 4 Bertha-road, Neutral Bay.
1919	P 1	Waterhouse, Lionel Lawry, B.E. <i>Syd.</i> , Lecturer and Demonstrator in Geology in the University of Sydney.
1919	P 6	Waterhouse, Walter L., M.C., D.Sc.Agr., D.I.C., F.L.S., Reader in Agriculture, University of Sydney; p.r. "Hazelmere," Chelmsford-avenue, Lindfield. (President, 1937.)
1941	P 1	Watson, Irvine Armstrong, Ph.D., B.Sc.Agr., Assistant Lecturer, Faculty of Agriculture, University of Sydney.
1911	P 1	Watt, Robert Dickie, M.A., B.Sc., Professor of Agriculture in the University of Sydney; p.r. 64 Wentworth-road, Vaucluse. (President, 1925.)
1936		Wearne, Harold Wallis, 22 Yarabah-avenue, Gordon.
1920	P 1	Wellish, Edward Montague, M.A., Associate-Professor of Applied Mathematics in the University of Sydney; p.r. 15 Belgium-avenue, Roseville.
1921		Wenholz, Harold, B.Sc.Agr., Director of Plant Breeding, Department of Agriculture, Sydney.
1909	P 3	†White, Charles Josiah, B.Sc., Lecturer in Chemistry, Teachers' College, University Grounds, Newtown.
1940	P 1	White, Douglas Elwood, M.Sc., D.Phil., University of Western Australia, Nedlands, W.A.
1943		Whiteman, Reginald John Nelson, M.B., Ch.M., F.R.A.C.S., 143 Macquarie-street, Sydney.
1928		Wiesener, Frederick Abbey, M.B., Ch.M., D.O.M.S., Ophthalmic Surgeon, 143 Macquarie-street, Sydney; p.r. Jersey-road, Strathfield.
1942		Williams, Gordon Roy, B.Sc., 45 Conder-street, Burwood.

Elected.

1943		Winch, Leonard, B.Sc., Chief Chemist, Fielder's General Products Ltd., P.O. Box 143, Tamworth, N.S.W.
1940		Wogan, Samuel James, Range-road, Sarina, North Queensland.
1936	P 2	Wood, Harley Weston, M.Sc., A.Inst.P., F.R.A.S., Assistant Astronomer, Sydney Observatory.
1906	P 12	†Woolnough, Walter George, D.Sc., F.G.S., 9 Lockerbie Court, East St. Kilda, Victoria. (President, 1926.)
1916		Wright, George, Company Director, c/o Hector Allen, Son & Morrison, 16 Barrack-street, Sydney; p.r. "Wanawong," Castle Hill, N.S.W.
1921		Yates, Guy Carrington, Seedsman, c/o Arthur Yates & Co. Ltd., 184 Sussex-street, Sydney; p.r. Boomerang-street, Turramurra.

HONORARY MEMBERS.

Limited to Twenty.

Elected.

1914		Hill, James P., D.Sc., F.R.S., Professor of Zoology, University College, Gower-street, London, W.C.1, England.
1915		Maitland, Andrew Gibb, F.G.S., "Bon Accord," 28 Melville-terrace, South Perth, W.A.
1912		Martin, Sir Charles J., C.M.G., D.Sc., F.R.S., Roebuck House, Old Chesterton, Cambridge, England.
1922		Wilson, James T., M.B., Ch.M. <i>Edin.</i> , F.R.S., Professor of Anatomy in the University of Cambridge: p.r. 24 Millington-road, Cambridge, England.

OBITUARY, 1943-1944.
Elected.

- 1922 John Job Crew Bradfield.
 1936 Archibald Howie.
 1940 James Edward Mills
 1939 Frederick Chapman. (Honorary Member.)
-

THE REV. W. B. CLARKE MEMORIAL FUND.

The Rev. W. B. Clarke Memorial Fund was inaugurated at a meeting of the Royal Society of N.S.W. in August, 1878, soon after the death of Mr. Clarke, who for nearly forty years rendered distinguished service to his adopted country, Australia, and to science in general. It was resolved to give an opportunity to the general public to express their appreciation of the character and services of the Rev. W. B. Clarke "as a learned colonist, a faithful minister of religion, and an eminent scientific man." It was proposed that the memorial should take the form of lectures on Geology (to be known as the Clarke Memorial Lectures), which were to be free to the public, and of a medal to be given from time to time for distinguished work in the Natural Sciences done in or on the Australian Commonwealth and its territories; the person to whom the award is made may be resident in the Australian Commonwealth or its territories, or elsewhere.

The Clarke Memorial Medal was established first, and later, as funds permitted, the Clarke Memorial Lectures have been given at intervals.

CLARKE MEMORIAL LECTURES.

Delivered.

1906. "The Volcanoes of Victoria," and "The Origin of Dolomite" (two lectures). By Professor E. W. Skeats, D.Sc., F.G.S.
1907. "Geography of Australia in the Permo-Carboniferous Period" (two lectures). By Professor T. W. E. David, B.A., F.R.S.
"The Geological Relations of Oceania." By W. G. Woolnough, D.Sc.
"Problems of the Artesian Water Supply of Australia." By E. F. Pittman, A.R.S.M.
"The Permo-Carboniferous Flora and Fauna and their Relations." By W. S. Dun.
1918. "Brain Growth, Education, and Social Inefficiency." By Professor R. J. A. Berry, M.D., F.R.S.E.
1919. "Geology at the Western Front." By Professor T. W. E. David, C.M.G., D.S.O., F.R.S.
1936. "The Aeroplane in the Service of Geology." By W. G. Woolnough, D.Sc. (THIS JOURN., 1936, 70, 39.)
1937. "Some Problems of the Great Barrier Reef." By Professor H. C. Richards, D.Sc. (THIS JOURN., 1937, 71, 68.)
1938. "The Simpson Desert and its Borders." By C. T. Madigan, M.A., B.Sc., B.E., D.Sc. (Oxon.). (THIS JOURN., 1938, 71, 503.)
1939. "Pioneers of British Geology." By Sir John S. Flett, K.B.E., D.Sc., LL.D., F.R.S. (THIS JOURN., 1939, 73, 41.)
1940. "The Geologist and Sub-surface Water." By E. J. Kenny, M.Aust.I.M.M. (THIS JOURN., 1940, 74, 283.)
1941. "The Climate of Australia in Past Ages." By C. A. Sussmilch, F.G.S. (THIS JOURN., 1941, 75, 47.)
1942. "The Heroic Period of Geological Work in Australia." By E. C. Andrews, B.Sc.
1943. "Australia's Mineral Industry in the Present War." By H. G. Raggatt, D.Sc.

AWARDS OF THE CLARKE MEDAL.

Established in memory of

The Revd. WILLIAM BRANWHITE CLARKE, M.A., F.R.S., F.G.S., etc.

Vice-President from 1866 to 1878.

The prefix * indicates the decease of the recipient.

Awarded.

- 1878 *Professor Sir Richard Owen, K.C.B., F.R.S.
- 1879 *George Bentham, C.M.G., F.R.S.
- 1880 *Professor Thos. Huxley, F.R.S.
- 1881 *Professor F. M'Coy, F.R.S., F.G.S.
- 1882 *Professor James Dwight Dana, LL.D.
- 1883 *Baron Ferdinand von Mueller, K.C.M.G., M.D., Ph.D., F.R.S., F.L.S.
- 1884 *Alfred R. C. Selwyn, LL.D., F.R.S., F.G.S.
- 1885 *Sir Joseph Dalton Hooker, O.M., G.C.S.I., C.B., M.D., D.C.L., LL.D., F.R.S.
- 1886 *Professor L. G. De Koninck, M.D.
- 1887 *Sir James Hector, K.C.M.G., M.D., F.R.S.

Awarded.

- 1888 *Rev. Julian E. Tenison-Woods, F.G.S., F.L.S.
 1889 *Robert Lewis John Ellery, F.R.S., F.R.A.S.
 1890 *George Bennett, M.D., F.R.C.S. *Eng.*, F.L.S., F.Z.S.
 1891 *Captain Frederick Wollaston Hutton, F.R.S., F.G.S.
 1892 *Sir William Turner Thiselton Dyer, K.C.M.G., C.I.E., M.A., LL.D., Sc.D., F.R.S., F.L.S.
 1893 *Professor Ralph Tate, F.L.S., F.G.S.
 1895 *Robert Logan Jack, LL.D., F.G.S., F.R.G.S.
 1895 *Robert Etheridge, Jnr.
 1896 *The Hon. Augustus Charles Gregory, C.M.G., F.R.G.S.
 1900 *Sir John Murray, K.C.B., LL.D., Sc.D., F.R.S.
 1901 *Edward John Eyre.
 1902 *F. Manson Bailey, C.M.G., F.L.S.
 1903 *Alfred William Howitt, D.Sc., F.G.S.
 1907 *Professor Walter Howchin, F.G.S., University of Adelaide.
 1909 *Dr. Walter E. Roth, B.A.
 1912 *W. H. Twelvvetrees, F.G.S.
 1914 Sir A. Smith Woodward, LL.D., F.R.S., Keeper of Geology, British Museum (Natural History), London.
 1915 *Professor W. A. Haswell, M.A., D.Sc., F.R.S.
 1917 *Professor Sir Edgeworth David, K.B.E., C.M.G., D.S.O., M.A., Sc.D., D.Sc., F.R.S., F.G.S.
 1918 *Leonard Rodway, C.M.G., Honorary Government Botanist, Hobart, Tasmania.
 1920 *Joseph Edmund Carne, F.G.S.
 1921 *Joseph James Fletcher, M.A., B.Sc.
 1922 *Richard Thomas Baker, The Crescent, Cheltenham.
 1923 *Sir W. Baldwin Spencer, K.C.M.G., M.A., D.Sc., F.R.S.
 1924 *Joseph Henry Maiden, I.S.O., F.R.S., F.L.S., J.P.
 1925 *Charles Hedley, F.L.S.
 1927 Andrew Gibb Maitland, F.G.S., "Bon Accord," 28 Melville Terrace, South Perth, W.A.
 1928 Ernest C. Andrews, B.A., F.G.S., 32 Benelong Crescent, Bellevue Hill.
 1929 Professor Ernest Willington Skeats, D.Sc., A.R.C.S., F.G.S., University of Melbourne, Carlton, Victoria.
 1930 L. Keith Ward, B.A., B.E., D.Sc., Government Geologist, Geological Survey Office, Adelaide.
 1931 *Robin John Tillyard, M.A., D.Sc., Sc.D., F.R.S., F.L.S., F.E.S., Canberra, F.C.T.
 1932 Frederick Chapman, A.L.S., F.R.S.N.Z., F.G.S., Melbourne.
 1933 Walter George Woolnough, D.Sc., F.G.S., Department of the Interior, Canberra, F.C.T.
 1934 *Edward Sydney Simpson, D.Sc., B.E., F.A.C.I., Carlingford, Mill Point, South Perth, W.A.
 1935 George William Card, A.R.S.M., 16 Ramsay-street, Collaroy, N.S.W.
 1936 Sir Douglas Mawson, Kt., O.B.E., F.R.S., D.Sc., B.E., University of Adelaide
 1937 J. T. Jutson, B.Sc., LL.B., 9 Ivanhoe-parade, Ivanhoe, Victoria.
 1938 Professor H. C. Richards, D.Sc., The University of Queensland, Brisbane.
 1939 C. A. Susasmilch, F.G.S., F.S.T.C., 11 Appian Way, Burwood, N.S.W.
 1941 Professor Frederic Wood Jones, M.B., B.S., D.Sc., F.R.S., Anatomy Department, University of Manchester, England.
 1942 William Rowan Browne, D.Sc., Reader in Geology, The University of Sydney, N.S.W.
 1943 Walter Lawry Waterhouse, M.C., D.Sc.Agric., D.I.C., F.L.S., Reader in Agriculture, University of Sydney.

AWARDS OF THE SOCIETY'S MEDAL AND MONEY PRIZE.

Money Prize of £25.

Awarded.

- 1882 John Fraser, B.A., West Maitland, for paper entitled "The Aborigines of New South Wales."
 1882 Andrew Ross, M.D., Molong, for paper entitled "Influence of the Australian climate and pastures upon the growth of wool."

The Society's Bronze Medal and £25.

Awarded.

- 1884 W. E. Abbott, Wingen, for paper entitled "Water supply in the Interior of New South Wales."
 1886 S. H. Cox, F.G.S., F.C.S., Sydney, for paper entitled "The Tin deposits of New South Wales."
 1887 Jonathan Seaver, F.G.S., Sydney, for paper entitled "Origin and mode of occurrence of gold-bearing veins and of the associated Minerals."
 1888 Rev. J. E. Tenison-Woods, F.G.S., F.L.S., Sydney, for paper entitled "The Anatomy and Life-history of Mollusca peculiar to Australia."

Awarded.

- 1889 Thomas Whitelegge, F.R.M.S., Sydney, for paper entitled "List of the Marine and Fresh-water Invertebrate Fauna of Port Jackson and Neighbourhood."
 1889 Rev. John Mathew, M.A., Coburg, Victoria, for paper entitled "The Australian Aborigines."
 1891 Rev. J. Milne Curran, F.G.S., Sydney, for paper entitled "The Microscopic Structure of Australian Rocks."
 1892 Alexander G. Hamilton, Public School, Mount Kembla, for paper entitled "The effect which settlement in Australia has produced upon Indigenous Vegetation."
 1894 J. V. De Coque, Sydney, for paper entitled the "Timbers of New South Wales."
 1894 R. H. Mathews, L.S., Parramatta, for paper entitled "The Aboriginal Rock Carvings and Paintings in New South Wales."
 1895 C. J. Martin, D.Sc., M.B., F.R.S., Sydney, for paper entitled "The physiological action of the venom of the Australian black snake (*Pseudechis porphyriacus*)."
 1896 Rev. J. Milne Curran, Sydney, for paper entitled "The occurrence of Precious Stones in New South Wales, with a description of the Deposits in which they are found."
 1943 Edwin Cheel, Sydney, in recognition of his contributions in the field of botanical research and to the advancement of science in general.

 AWARDS OF THE WALTER BURFITT PRIZE.

Bronze Medal and Money Prize of £50.

Established as the result of a generous gift to the Society by Dr. W. F. BURFITT, B.A., M.B., Ch.M., B.Sc., of Sydney. Awarded at intervals of three years to the worker in pure and applied science, resident in Australia or New Zealand, whose papers and other contributions published during the past three years are deemed of the highest scientific merit, account being taken only of investigations described for the first time, and carried out by the author mainly in these Dominions.

Awarded.

- 1929 Norman Dawson Royle, M.D., Ch.M., 185 Macquarie Street, Sydney.
 1932 Charles Halliby Kellaway, M.C., M.D., M.S., F.R.C.P., The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.
 1935 Victor Albert Bailey, M.A., D.Phil., Associate-Professor of Physics, University of Sydney.
 1938 Frank Macfarlane Burnet, M.D. (*Melb*), Ph.D. (*Lond.*), The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.
 1941 Frederick William Whitehouse, D.Sc., Ph.D., University of Queensland, Brisbane.

 AWARDS OF LIVERSIDGE RESEARCH LECTURESHIP.

This Lectureship was established in accordance with the terms of a bequest to the Society by the late Professor Archibald Liversidge. Awarded at intervals of two years, for the purpose of encouragement of research in Chemistry. (THIS JOURNAL, Vol. LXII, pp. x-xiii, 1928.)

Awarded.

- 1931 Harry Hey, c/o The Electrolytic Zinc Company of Australasia, Ltd., Collins Street, Melbourne.
 1933 W. J. Young, D.Sc., M.Sc., University of Melbourne.
 1940 G. J. Burrows, B.Sc., University of Sydney.
 1942 J. S. Anderson, B.Sc., Ph.D. (*Lond.*), A.R.C.S., D.I.C., University of Melbourne.

PRESIDENTIAL ADDRESS

By H. PRIESTLEY, M.D., Ch.M., B.Sc.

Delivered to the Royal Society of New South Wales, April 7, 1943.

PART I. THE PAST YEAR. 1956

The Society's activities have been carried on very much as usual. The Council meetings and general monthly meetings have been held regularly. One of the few departures from the normal was an alteration in the times of the general monthly meetings. In an attempt to meet the difficulties which, it was anticipated, would be caused by "blackout" conditions, afternoon and early evening meetings were held. The change was not a popular one, and it was decided to return to the usual time of 7.15. For the same reason no Popular Science Lectures were given during the winter months; instead, a series of Popular Science Talks were broadcast from the national stations during the month of July. This was in the nature of an experiment, but the possibility of continuing such broadcast talks, as well as arranging the usual series of Popular Science Lectures, is being considered. The Society's thanks are due to those who gave considerable time and thought to the preparation and delivery of these talks.

The membership of the Society stands at 292, a slight decrease from that of last year. Six members have resigned, seven new members have been elected, while seven members have died. We regret to announce the death of Marcus Baldwin Welch, who had been a member since 1920, and who contributed many papers to the Society. He was a member of the Council from 1932 to 1938, and again from 1939 to 1941, during which time he was Honorary Treasurer. Another death we regret to announce is that of Archibald Durrant Ollé, who was a member since 1913 and was chairman of the Section of Industry for several years. Other members lost by death are John Clifford Firth, elected in 1935, Gerald Harnett Halligan, elected in 1880, James Adam Dick, elected in 1894, Sir Kelso King, elected in 1896, and finally, Professor Sir J. J. Thomson, an honorary member since 1915.

Despite the war, with its preoccupations and the extra duties that most workers in science have undertaken, either in the form of special researches or extra lectures owing to short staffs, the number of research papers presented before the Society was 28, an improvement on the number of papers read last year.

In July a very successful symposium was held on the subject of Rubber. A large number of members and visitors attended, and a discussion took place after the addresses had been heard.

A special celebration was that of the commemoration of the tercentenary of the death of Galileo and the birth of Newton, when an address was delivered at the meeting in October by Professor O. U. Vonwiller. The address, "Galileo and Newton: Their Times and Ours", has been printed in the Journal and Proceedings.

Of the several foundations administered by the Royal Society of New South Wales, the following activities may be reported :

The Clarke Memorial Lecture was delivered by Mr. E. C. Andrews, a member of long standing and a former President of the Society, his subject being "The Heroic Period of Geological Work in Australia".

The Clarke Memorial Medal was awarded to Dr. W. R. Browne, Reader in Geology of the University of Sydney.

The Society invited Dr. J. S. Anderson, of the Chemistry School, University of Melbourne, to visit Sydney, in order to deliver two lectures under the Liversidge Research Grant. Dr. Anderson's subjects were "The Chemistry of the Earth" and "The Imperfect Crystal", and the lectures were given on October 27th and 29th respectively.

A task to which a great deal of time has been devoted during the past year by the committee appointed for the purpose was the revision of the rules. A close examination and comparison of some of the rules revealed both contradictions and inconsistencies, which it has been the endeavour of the committee to remove. Provision has been made, among other alterations, for absentee voting for new office-bearers and members of Council. The period of years qualifying for life membership has been reduced from forty years to thirty-five, thus bringing in a number of new life members whose loyalty to the Society throughout many years is thus rewarded.

The finances of the Society are in a satisfactory state, as shown by the Annual Balance Sheet and Revenue Account. We have endeavoured to do our part in the war effort by subscribing or converting amounts totalling £1,400 to war loans during the past twelve months.

The policy of inviting applications for grants for research, for which provision is made in our rules, has been under consideration : a grant of £50 for 1943 has been made to the Australian National Research Council for the furtherance of scientific research.

We acknowledge with grateful thanks the subsidy of £400 for the year 1943 from the Government of New South Wales.

The thanks of the members of the Society and myself are due to the Honorary Secretaries, Professor Elkin and Mr. Mellor, for their work in keeping the wheels running smoothly ; Mr. Mellor also has undertaken the onerous task of editing the Journal and Proceedings, a work so ably carried out for a number of years by Dr. C. Anderson, who owing to important war work found himself obliged to resign from the post of Joint Secretary and Editor. Our thanks are due also to the Honorary Treasurer, Mr. Clunies Ross, to Mr. J. A. Dulhunty, Assistant Editor, and to Mr. Maze and Dr. Bolliger, the Honorary Librarians, who have continued their efforts to increase the usefulness of the library.

PART II. LIFE AND LIVING.

Sir Gowland Hopkins has expressed very well the place of biochemistry in the study of life processes.

"Physiology as ordinarily understood is chiefly concerned in every case with the visible functioning of organs ; biochemistry rather with the molecular events which are associated with these visible activities. I venture to think that productive thought in biochemistry in particular calls for the widest possible survey of life's manifestations. One of its ultimate tasks is to decide on what, from the chemical standpoint, is essential for these manifestations as distinct from what is secondary and specific. For any such decisions the necessary harvest of contributory facts must come from many diverse fields."

In a very searching essay published in 1939 in "Perspectives in Biochemistry", N. W. Pirie discusses "The Meaninglessness of the Terms, Life

and Living". I hope to show that, incomplete as our knowledge is in most directions, we can give some meaning to the terms. I shall develop the idea that a living system is an everchanging and dynamic, but at the same time organised and coordinated assemblage of enzyme systems which, under suitable conditions, is able to synthesise, from simpler substances, the whole or part of each enzyme system of the assemblage.

Death results from disorganisation of the assemblage beyond a certain degree which may result from either physical means or the removal of the activity of one or more of the enzyme systems by the action of some foreign substance or the lack of substrates.

There is involved here the idea that the cell protoplasm has a definite organised structure with a certain limited degree of freedom of alteration of structural pattern and is not simply a heterogeneous collection of substances in the colloidal and crystalloidal state.

It is certain that almost all chemical changes taking place in living organisms are brought about by enzyme action.

We may define an enzyme as an organic catalyst, probably always a protein or containing a protein, which brings about in a smooth and orderly fashion, specific chemical changes in a substrate, the substance upon which it acts, such as the addition or removal of such groups as H, PO_4 , H_2O and many others. Each enzyme is, so far as we know, specific, not only for the particular grouping it immediately affects, but also the general chemical constitution of the molecule of the substrate or substrates. The product of the enzyme action may be modified by subsequent non-enzymic chemical change. For example, amino acid oxidase removes hydrogen converting the amino acid into an imino acid which subsequently by non-enzymic action loses nitrogen and hydrogen and takes up oxygen to become a keto acid.

Green (1941) expands the definition of an enzyme to "Any protein which *uniquely* performs some specialised physiological function". One has then of course to define what is meant by specialised physiological function. Green would include visual purple, specific for photoreception in the retina, and haemoglobin, specific for the transfer of oxygen, as enzymes.

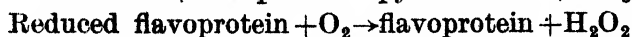
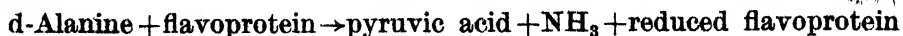
Enzymes such as pepsin and trypsin may be produced by living cells and passed out of the cells into the environment, but we shall not concern ourselves with these here except to indicate that they are the products of cell activity. It is the intracellular enzyme systems that I wish to consider here.

Very many enzyme systems have been isolated during the past few years from bacteria, yeast, plant and animal cells. Some of these have been obtained in crystalline and relatively pure form, others in an impure state only, but more or less separated from other enzymes.

A great deal is known about the oxidative enzymes of cells which use as substrates carbohydrates or derivatives of carbohydrates such as pyruvic acid, citric acid, succinic acid and very many others. Very little is known yet about the enzyme systems of cells which are concerned with the breakdown and building up of lipids and proteins.

All the oxidative enzyme systems seem to be made up of a specific protein and a non-protein or prosthetic group attached more or less firmly to the protein. The prosthetic groups vary greatly in composition and complexity from simple metals like copper to complex substances like flavin adenine dinucleotide and iron porphyrins. Each component of the enzyme is highly specific but the same prosthetic group may form a part of several different enzymes by being combined with different specific proteins. The prosthetic group acts, at least in many cases, as a cyclic carrier being alternately reduced and oxidised. Thus consider the action of the d-amino acid oxidase isolated from liver. This is a specific protein combined with flavin adenine dinucleotide.

The prosthetic group here is reduced by the alanine which is simultaneously oxidised and then oxidised by molecular oxygen so that it is available to repeat the cycle.



In most cases the reaction is not as simple as this, there being 2, 3, 4 or more systems between the substrate and molecular oxygen. The only chemical change here is the transfer of 2 H atoms from the substrate to molecular oxygen and this takes place through the prosthetic group. The action of the specific protein part is essential but obscure. It is said to "activate" the substrate so that 2 H atoms can easily split off. This of course does not take us very far. There is evidence that the substrate in some way combines with the specific protein and the transfer of hydrogen takes place from the substrate to the prosthetic group in the complex substrate-specific protein-prosthetic group. Since water is essential for the process it is possible that the transfer is more complex than that indicated.

As I wish to consider the action of vitamins and drugs on cellular activities, it will be of interest to see what are the substances which are known to play the parts of prosthetic groups.

The simplest enzyme systems from this point of view are the metallo-proteins where a simple metal acts as the prosthetic group. The best known of these are copper-proteins. The polyphenol oxidases of fungi and various higher plants as the potato, the monophenol oxidases of fungi and ascorbic acid oxidase of the cucumber belong here.

Of more interest are the enzyme systems where one prosthetic group combined with different specific proteins gives different enzyme systems. Flavin-adenine dinucleotide is such a substance (Figure I).

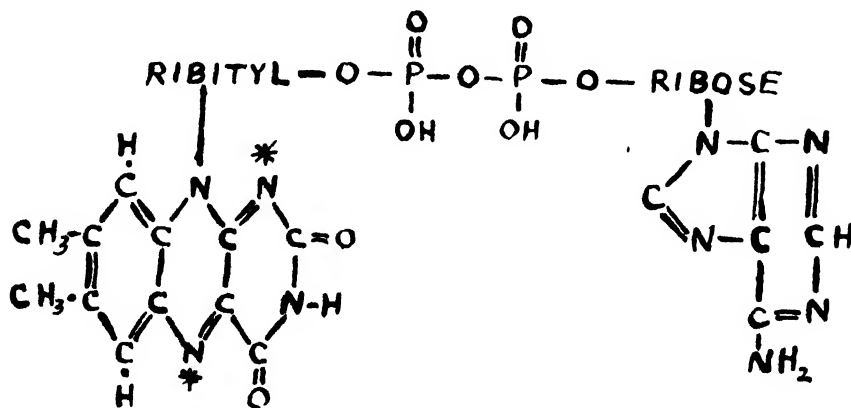


Fig. I.

Here oxidation reduction changes take place on the nitrogens marked *. Enzyme systems bringing about the oxidation of d-amino-acids, purines, aldehydes, dihydrocoenzyme I and dihydrocoenzyme II are known. Two systems are known where the flavin phosphate is present without the adenine. Some of these are possibly artefacts and there is evidence that they may not exist within the living cell.

Another important group contains as prosthetic group one of the pyridine dinucleotides, diphosphopyridin dinucleotide (Figure II) or triphosphopyridine dinucleotide which has another phosphoric acid group. These are specifically different. A number of enzyme systems containing diphosphopyridine nucleotide

(D.P.N.) (Coenzyme I), are known, including enzymes which oxidise, respectively, alcohol, aldehyde, lactate, malate, triose, glucose, glycerophosphate, β hydroxybutyrate, glutamate and formate. Enzyme systems containing T.P.N. (Coenzyme II) are less numerous. Among them are systems oxidising hexose monophosphate, isocitrate, glutamate and glucose. Each of these dozen or more enzyme systems contains a different protein and is specific to the one substrate.

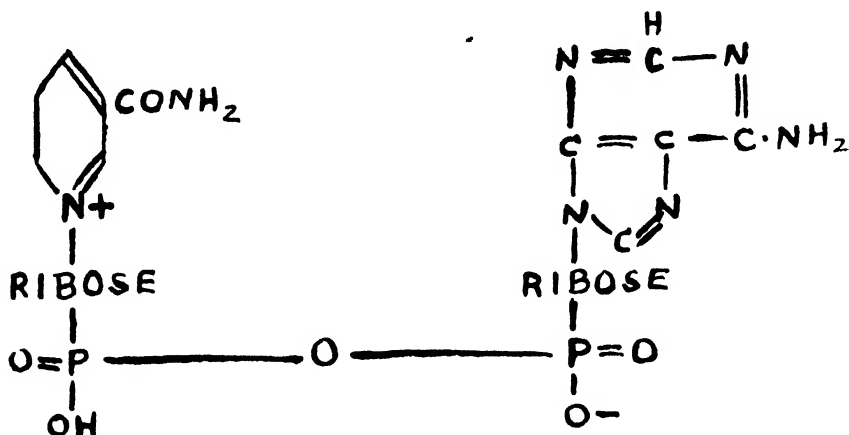
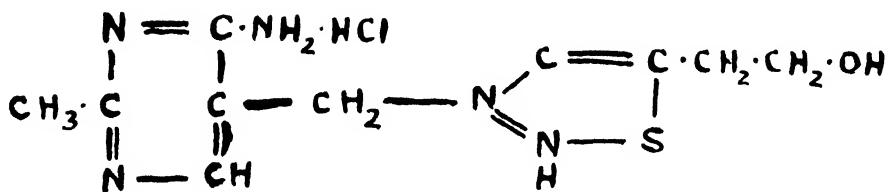


Fig. II.

Systems containing an ironporphyrin are very important in most cells, plant and animal. Among these are the cytochromes, catalase, peroxidase and possibly cytochrome oxidase.

Thiamine diphosphate combined with a specific protein and a metal usually magnesium forms a number of enzyme systems which are of particular importance in the oxidation of ketoacids. Carboxylase of yeast is the best known of these enzymes but in animal tissues there is a diphosphothiamin system which oxidises ketoglutarate to succinate. Diphosphothiamin also catalyses carbohydrate synthesis from pyruvate or rather some step in this process, citrate synthesis from pyruvate and oxalacetate, synthesis of succinic acid and synthesis of aceto-acetate.



thiamin chloride hydrochloride.

Fig. III.

An indication of the many ways the same prosthetic group with different specific proteins may act is given in the following table by Stern (1940)—the known biological reactions involving thiamindiphosphate with pyruvic acid (P.A.) as the substrate.

A number of other similar enzyme systems are known in cells from various sources but nothing is known about their nature. There is evidence that ascorbic acid plays an important part in some enzyme systems particularly synthetic. There is much evidence to show that p-amino benzoic acid is essential for some enzymic processes in cells from many sources but how it acts is not

Reaction.	Material.	Conditions.
PA → Acetaldehyde + CO ₂	Yeast.	Aerobic, anaerobic.
PA + 5/2 O ₂ → 3CO ₂ + 2H ₂ O	Brain.	Aerobic.
PA + 1/2 O ₂ → Acetic acid + CO ₂	{ Brain.	Aerobic.
	{ Gonococcus.	
2PA + H ₂ O → Lactic acid + Acetic acid + CO ₂ ..	{ Gonococcus.	Anaerobic.
	{ Brain.	Aerobic.
PA + 2H → Lactic acid	{ Muscle.	{ Anaerobic.
		{ Aerobic.
	{ Tumour.	{ Anaerobic.
		{ Aerobic.
PA + Oxalacetic acid → Citric acid	Muscle.	Anaerobic.
2PA → Acetic acid + Formic acid	Streptococcus.	Anaerobic.
PA + Glutamic acid → Alanine + α-ketoglutaric acid		
2PA → Succinic acid → Fumaric acid → Malic acid → Oxalacetic acid → PA + CO ₂	Muscle.	Anaerobic.
PA + H ₂ O ₂ → Acetic acid + CO ₂ + H ₂ O	Kidney cortex.	Aerobic.
2PA → Acetoacetic acid	Pneumococcus.	Aerobic.
2PA → β-Hydroxybutyric acid	Liver.	Aerobic.
2PA → Succinic acid	Muscle.	Anaerobic.
PA → Pyruvic acid	Testis.	Anaerobic.

known. The importance of this will be seen later in the discussion on the effect of certain drugs on cell metabolism.

The catalytic efficiencies of the different protein-prosthetic group enzymes vary very much as is indicated by their turn-over numbers, that is the number of oxidation-reduction cycles undergone per minute by the prosthetic group, or the number of substrate molecules oxidised per minute by one molecule of enzyme. Thus the flavin adenine dinucleotide protein which brings about oxidation of dihydrocoenzyme II has a turn over number of 220, the diphosphopyridine protein which oxidises alcohol to aldehyde has a turn over number of 20,000 at 20° C., while catalase which splits off oxygen from peroxides has a turn over number of 2,640,000 at 0° C.

The firmness of attachment of the prosthetic group to the specific protein varies very greatly and there is considerable evidence that a particular prosthetic group may leave one protein and attach itself to another if various conditions are changed. The systems so far considered are oxidation-reduction systems concerned with the transfer of electrons finally to molecular oxygen and the simultaneous liberation of energy.

In very few cases is there only one enzyme system between the substrate and molecular oxygen. Generally there are 3, 4 or more such systems, those nearest to the substrate having a more negative oxidation-reduction potential, those near oxygen having a more positive oxidation-reduction potential under the existing conditions.

Thus

Substrate + activating protein

+

Coenzyme I —————→ Flavinadenine dinucleotide protein
(Diaphorase I)

————→ (Cytochromes) —————→ Cytochrome oxidase —————→ O₂

Oxidations of this type can be followed quite readily in isolated systems *in vitro* but they can be greatly accelerated by the simultaneous action of other systems not specifically concerned with oxidations and reduction. In particular

the participation of phosphorylation processes has been much studied during the last few years and shown to be of very great importance. In a recent review Fritz Lipmann (1941) has discussed the parts played by phosphorylation and dephosphorylation in many enzymic processes which may take place in cells. Thus the conversion of glucose to glycogen and *vice versa* is always associated with phosphorylations, the oxidation of glucose and of trioses is probably always as their phosphorylated compounds. We have seen that most of the prosthetic groups considered contain phosphoric acid but in addition adenosine triphosphate, creatine phosphate and, in some animals, arginine phosphate are also necessary as sources of phosphoric acid radicles. Quite a considerable part of the energy exchanges in cells can and does come from changes in phosphoric acid bonding.

Of other enzyme systems in cells not a great deal is known at present excepting the actions of certain of them in isolated systems. Thus several proteolytic enzymes and peptidases have been isolated from cells from various sources. The specificity and kinetics of these enzyme systems have been studied but not much information has been obtained which can be used in considering the reactions within the living cell. Claims have been made for the synthesis of proteins by proteolytic enzymes from simpler peptides but I have repeated most of the work and cannot satisfy myself that proteins are formed. A consideration of energy requirements shows the great unlikelihood of such synthesis *in vitro* in isolated systems. Behrens and Bergmann (1939) have shown that the peptide linkage can be formed in homogeneous solution *in vitro* by papain.

Many workers have shown the importance of the sulphydryl group in the proteolytic enzymes of cells. When this is oxidised to the disulphide the enzymes become inactive. Reduction and activation can be brought about in many cases by cyanides and cysteine. Fruton and Bergmann (1940) consider that the cyanide forms a prosthetic group and consider that glutathione may act in the same way within cells.

The proteolytic enzymes are proteins, but excepting possibly for the foregoing no prosthetic groups have been found.

Very little indeed is known about cell lipases and esterases and almost nothing about the enzymes concerned with the synthesis and breakdown of fatty acids.

Many other enzyme systems have been demonstrated in cells from various sources and it is certain that we are nowhere near knowing all the enzymes in any one cell.

It is evident then that living cells contain a great number of different enzymes catalysing very many different chemical reactions. Within the cell there must be considerable interaction between different enzyme systems the product of one enzyme system being the substrate of another. Many of these are known *in vitro* with extracts of the cells, but whether any of these actually occur within cells is not certain.

It will be observed that little has been said about synthetic processes. Synthesis of complex organic substances from simple substances is one of the most characteristic activities of living cells. For synthesis to occur we almost always require the intact living cell and so far it has not been possible to study in any detail particular synthetic processes among all the complex associations within the living cell. Not only do synthetic processes require the intact cell but so also do some oxidising processes. For example, surviving slices of liver with intact cells will oxidise fatty acids, but this property is lost so soon as the tissue is minced. The oxidation of the l-series of amino-acids requires the intact cell.

Further, most complex substances synthesised in cells have a higher energy content than the substances from which they were synthesised, so energy must

be provided at the right time and in the right place to enable synthesis to go on, that is there must be coupled with the synthetic process other systems which provide energy by oxidation or in some other way.

Thus Borsook and Jeffreys (1935) calculate that the net change of free energy in the synthesis of urea from ammonia, acid and carbon dioxide is +14,300 calories. Krebs (1935) has demonstrated that the synthesis of urea in the liver can go on only with the simultaneous oxidation of some substrate—glucose or lactic acid. Similarly Krebs (1935) has shown that the synthesis of glutamine is, under physiological conditions, an endothermic reaction. In the kidney and brain the energy required is derived from oxidation of some substrate. Extracts of tissues which synthesise glutamine contain an enzyme which splits glutamine into glutamic acid and ammonia, a reaction which does not take place with the living tissue. There is considerable evidence that this glutaminase is the same enzyme which, under the conditions existing in the living cell, brings about synthesis of glutamine. Glycogen and starch can be synthesised in small amounts from glucose-1-phosphate by extracts of suitable animal or vegetable tissues, which of course are mixtures of various enzyme systems and substrates, while in the intact cell the reaction may go almost wholly in the direction glucose→glycogen or starch, but can be reversed.

The methods by which couplings of energy are accomplished in living cells is very obscure but has something to do with the structural disposition of the enzyme systems within the cell. It is evident that the structure of the living protoplasm is not a mere static condition of cell substance but an active, dynamic, condition necessary for the uninterrupted transfer of energy. The energy yielding system must be very close to, if not actually in contact with, the energy receiving system.

A number of Russian biochemists, in particular Oparin and Kurssanov (1941), have advanced the thesis, and supported it by much evidence, that in the living cell a part of an enzyme exists in solution and exerts a hydrolytic action only, and a part is adsorbed to the water poor, plasmatic structure and works only by synthesis. The relative proportion between the enzyme distribution in the watery phase and that adsorbed on the structural phase depends on certain physico-chemical and energetic relations within the cell. The ratio of speed of synthesis and hydrolysing action, or the prevailing direction of the enzymic process, in the cell, depends on the quantitative relations between the structurally bound and the free enzyme and also on the availability of adequate energy for the synthesis.

Alterations in the prevailing direction of enzyme action in the cell can be caused by the influence of environmental factors on the inner condition of the cell as well as through inner causes.

Various authors have discussed the internal structural organisation of cell protoplasm. R. A. Peters (1939) suggests a cytoskeleton consisting of three parts, surface proteins, cytoplasmic proteins and nuclear proteins. He likens it to the nervous system with nuclear protein corresponding to the central nervous system, to conducting units the cytoplasmic protein and to the surface protein the rôle of acceptor or receptor. He makes no suggestions as to the possible structure of such a cytoskeleton and concerns himself mainly with problems of transmission of effects from the surface to nuclear proteins or *vice versa*. A much more detailed theory as to the structure of cytoplasm in terms of native proteins has been developed by Dorothy Wrinch (1941). Briefly she summarises the idea as follows: "Recent work on native proteins . . . yields a picture of the native protein as consisting of isolated or associated molecular units, having rigid globular structures, on the surface of which some or all the R groups are rooted in definite spatial patterns. On this basis a new picture is suggested for the structure of cytoplasm, consisting of interlacing

native protein frameworks to which fats, carbohydrates, water and other foreign molecules are attached, located in an immense interpenetrating water phase, possibly with proteins in solution." She states that native proteins have, in general, very "sticky" surfaces, in the sense that they readily interlink with foreign molecules of a variety of types. They have on their surfaces, patches which have a "specific stickiness" by means of which they can interlink preferentially with other individual proteins and with certain foreign molecules. These patches are apparently spaced on their surfaces so that other proteins are held in position within certain limits. Proteins so linked together can thus form rods or strands of some degree of stability. Bernal and Fankuchen (1937) as a result of X-ray examinations state that the molecule of tobacco virus is probably made of piles of submolecules of dimensions $22\text{\AA} \times 20\text{\AA} \times 20\text{\AA}$, somewhat smaller than the normal protein molecule. The molecules of different strains of tobacco virus and of cucumber virus have substantially the same general shapes and size and are made up of similar subunits but these are arranged somewhat differently in the different tobacco virus strains and more markedly so in the cucumber virus.

There is abundant evidence that proteins can form relatively stable associations with other proteins and with certain non-proteins, notably lipids. The specific nature of the associations, in other words the "specific stickiness", is well seen in antigen-antibody complexes.

As regards the structural arrangement of the proteins in the cytoplasm we have to remember that an active cell may contain 95% of water and yet have a definite form and a certain degree of rigidity. Wrinch (1941) suggests something of the nature of a diamond lattice of protein molecules joined together with a relatively immense interpenetrating water phase. She shows that such a structure will have some measure of rigidity and some tensile strength while at the same time showing plasticity and structural viscosity but allowing cytoplasmic streaming. The Wrinch model is to some extent based on the supposed cyclol structure of the globular proteins but this is not necessary for any other type of globular or three dimensional structure for the protein molecules could be fitted into a similar pattern. Many considerations lead to the belief that what we might call the "living" proteins are "globular" in nature and do not consist of simple peptide chains. The proteins which show the polypeptide chain structure are the fibrous proteins mostly extracellular and "dead". There are possibly exceptions here. The myosin of the muscle cell is fibrous but it is to serve a special function and is not an ordinary structural cytoplasmic protein.

A point of some importance, which does not seem to have been made before, is that the individual protein units of such a network as has been postulated need not, indeed cannot, all be the same. How far we are to consider any of the protein of the cytoplasm, whether in the interior or on the surface of the cell as purely structural, it is not possible to say. When one considers the immense variety of enzyme proteins in the cytoplasm of any one cell and the fact that many enzyme activities are conditional on the integrity of the cell, it seems apparent that much, if not most, of the structural protein has enzymic properties or at least has enzyme proteins more or less firmly attached to it. One point must be stressed. There is no such thing as cytoplasmic protein as a single entity. The cytoplasm contains a great variety of different proteins many of which are enzyme proteins, others possibly purely structural or playing some part which is neither strictly structural nor strictly enzymic.

In this connection it has been shown by Engelhardt and Lyubimova (1939) that myosin, or some substance at present indistinguishable from it, acts enzymatically in the dephosphorylation of adenosine triphosphate to diphosphate. Needham *et al.* (1941), in confirming this, have suggested a theory of muscle

contraction in which adenosine triphosphate gives phosphorus to myosin—the phosphorylated myosin being the extended form. On stimulation the extended myosin phosphate liberates phosphate ions and contracts.

The distribution of different proteins has been much more actively studied in the nucleus than in the cytoplasm. Caspersson (1940) has shown that nuclei contain protamines, histones and probably proteins of a globulin nature. These three types of protein are found in the chromosomes.

Chromosomes show a banded structure or rather alternate areas which show respectively staining by various stains and absorption of ultra-violet rays on the one hand and absence of these properties on the other hand. The first areas have much nucleic acid, the second little or none. Caspersson has shown that the nucleoprotein bands have possibly all three of protamine, histone and globulin types; in the interband spaces chiefly globulin and protamine types and chiefly histone type in the nucleoli and the related puff and chromocentral regions. The linear pattern of the chromosomes is most likely due to the protamine type. Protamines are of the polypeptide chain type, ideally suitable for a linear arrangement. Mazia (1941) has shown that some chromosomes contain a relatively large amount of "matrix" protein which is digestible by pepsin, while the "skeletal" protein is not digested. Plant chromosomes, so far examined, show little of this "matrix" protein.

The chromosome may be pictured as a protamine-like thread, with nucleoprotein at intervals and a sheath of more complex protein related to the nucleolus and in some cases, if not all, a complex matrix protein.

There are two types of nucleic acid in nucleoproteins—ribose nucleic acids and deoxyribose nucleic acids depending on the sugar they contain. Ribose nucleic acids contain as the pyrimidine portion uracil, while deoxyribose nucleic acids contain the methylated derivative thymine. The principal nucleic acid in the chromosomes is deoxyribose nucleic acid, but there is some evidence that the bands of chromatin contain also ribose nucleic acid. The nucleolus definitely contains ribose nucleic acid. The nucleic acids appear to play a large, and possibly essential, part in protein synthesis in the nucleus and in the cytoplasm. The nucleic acid in the cytoplasm is of the ribose nucleic acid type and in cells which are functionally active or which are dividing rapidly the concentration of ribose nucleic acid is high. Claude (1941) claims that the greater part, if not all, the ribose nucleic acid in the cytoplasm is in the mitochondria as a nucleoprotein-phospholipid complex. Now the mitochondria have long been thought to play an important part in the production of enzymes such as pepsin and trypsin, which are manufactured in cell cytoplasm and pass from the cell. These are, of course, proteins. It is of interest also that in segmentation of the ovum, where the cell divides a number of times without increase in volume and so without increase in cytoplasmic protein, the ribose nucleic acid is small in amount.

The identification of the gene with a nucleoprotein seems to be generally accepted. Now during some phase of mitosis, probably the interphase, each gene duplicates itself, that is there is synthesis of the specific nucleoprotein of each gene. The gene nucleoprotein must then be looked upon as a synthesising enzyme. This is exactly paralleled by the power of virus proteins to reproduce themselves. A virus is a nucleoprotein with nucleic acid of the ribose type somewhat loosely attached to the protein. The protein part is not a protamine but is more complex, having a greater range of amino acids. Different strains of the tobacco virus have been shown by Stanley to differ in the relative amounts of the different amino acids, so the specificity of the different strains is evidently related to the make-up of the protein part. The whole virus can be looked upon as a protein synthesising enzyme. In the case of the gene there is simple

duplication, one gene makes another exactly like it. The same must be the case with the virus.

Now this idea of a protein synthesising itself and so being an enzyme must, it seems to me, be extended in a modified way to all the proteins in a cell, otherwise one is met with the difficulty of suggesting how the enzyme, itself a protein, which synthesises a protein is itself synthesised. Bergmann and Niemann (1937) have suggested that when an intracellular enzyme has at its disposal a number of protein fragments of different size and structure it subjects these fragments to a series of transformations and thereby reconstructs one peptide bond after another until there is produced a protein pattern which is stable in the presence of the enzyme. Proteinases should exist which have the ability of synthesising replicas of their own structural patterns. It seems to me that this idea demands a separate self-synthesising proteinase for the synthesis of each cell protein.

Delbruck (1941) has formulated a theory of short distance interaction, which does not attract the correct substrate, but which reduces its energy of oxidation, thus selecting the correct substrate for oxidation and thereby also for the synthesis. It would take too long to develop here the whole of his ideas which he applied to the duplication of chromosomes. The same process could, however, be applied to other cell proteins.

Concerning the action of ribose nucleic acid and the relation of the genes to cell synthesis, which of course must be very direct for the gene sets the pattern of the cell enzymes, it is of interest that the great increase in the cell cytoplasm preliminary to cell division takes place after the nuclear membrane has ruptured and the cytoplasm comes into very close relation with the chromosomes.

The action of viruses on the cell cytoplasm is also relevant here. The presence of virus protein in the cell cytoplasm is accompanied by changes in the enzymic activities of the cell in a variety of ways. Thus the variegations one so commonly sees in virus-infected plants must be due to the effect of the virus on the chlorophyll producing enzymic system.

The importance of nucleoproteins in cell enzyme systems is seen in the fact that many of the important oxidising enzymes are of the nature of nucleoproteins. Di- and tri-phosphopyridin nucleotides and flavin-adenin dinucleotide can be considered as particular types of nucleic acid. Adenosin triphosphate is a derivative of a nucleic acid.

The work of Schoenheimer and his co-workers on the use of labelled atoms has introduced quite radical changes in our ideas as to the stability of the protein molecule. By feeding rats with amino acids containing heavy nitrogen N_{15} or heavy nitrogen and deuterium they have been able to show that there is going on a very active exchange in nitrogen and hydrogen atoms in proteins throughout the body. When leucine containing N_{15} was fed over 50% of the N_{15} was retained in the body in proteins, although the animals were in nitrogenous equilibrium, so that according to current views there should be little protein synthesis proceeding. Further, the N_{15} was found not only in the leucine of the protein but also in most of the other amino acids, particularly glutamic and aspartic acids. This means that there is either a complete replacement of tissue protein by new synthesis every few days or that the peptide and other nitrogen linkages in the proteins can open, lose nitrogen, and have it replaced. The first seems impossible, the second means that proteins are exceedingly labile substances. These workers (Schoenheimer, Rattner and Rittenberg, 1939) consider that peptide links open, liberating amino acids which mix with others from whatever source. Some of these free amino acids re-enter directly into vacant positions left open by the rupture of peptide linkages, others transfer their nitrogen to deaminated molecules to form new amino acids, which in turn can enter the same chemical cycles. There does not seem any sound reason for postulating that amino acids as such are separated from the proteins and subse-

quently replaced by others of the same kind. It seems to me more likely that the fabric structure of the "living" protein is very labile and can open and lose nitrogen and carbon atoms from time to time and at different places. Indeed it is probable that the activity of "living" protein depends on this lability for, according to Rittenberg (1941), tendon, a "dead" protein, does not show the isotope replacement. Frey-Wyssling (1938) suggests that the function of nucleic acid is to "protect" the active side chains of the protein molecule. In view of what has been said as to the probable nucleoprotein nature of the gene and the relation of cytoplasmic nucleic acid to cytoplasmic protein synthesis, it seems not improbable that the nucleic acid may act by "protecting" the protein in making it less labile in the sense just discussed. It might be suggested that the specific enzymic activity of proteins is associated with their lability, while their ability to synthesise themselves is associated with the change in this lability brought about by the nucleic acid.

If, as has been postulated, the cell enzymes are largely arranged in a structural pattern, there should be restrictions within the living cell on various enzymic processes occurring in series in cell extracts where there is a large degree of freedom of movement of enzyme and substrate molecules. Small concentrations of cyanide will inhibit a large part, but not the whole of the respiration of living cells. Cyanide specifically poisons cytochrome oxidase, so there is evidently a part of the oxidation processes in the cell which does not go through this system. Ogston and Green (1935) find that the oxidation of hexose phosphate by intact yeast cells is cyanide-sensitive, but its oxidation by a system reconstructed from extracts of the same cell is relatively insensitive to cyanide. It is evident then that that part of the oxidation which, in the living cell, goes through cytochrome oxidase cannot be linked with the other system, probably a flavin protein system, so that there must be spatial separation between the systems.

Commoner and Thimann (1941) have shown that there is a relationship between growth and respiration in plants. In the *Avena* coleoptile, they have shown that the effectiveness of auxin as a growth hormone is related to the activation of a specific and small part of the total respiratory system (the four carbon dicarboxylic acids). The respiratory activity of the four carbon acids, oxaloacetic, malic, fumaric and succinic acids, which act as hydrogen carriers, is necessary for all of growth, but is responsible for only a small part of total respiration; when it is blocked, growth ceases entirely but the respiration rate falls only 10%. Here, too, there is evidence of specific orientation of the respiration systems.

In a recent article, which was seen after the greater part of this address was completed, Commoner (1942) discusses this point and states "It must be concluded that the cellular protoplasm is characterised by an interenzyme structure which plays the predominant rôle in determining the course of chemical events in the cell. The enzymes in the living cell are interrelated in such a manner as to constitute a relatively rigid structure which limits and orients the chemical activities which they carry out."

That the structural pattern can be altered and so bring about changes in cell metabolism is indicated by the changes which take place on fertilisation of ova. On fertilisation of marine ova one can see violent streaming and churning movements in the cytoplasm. Associated with these are usually marked alterations in the respiration rate.

Many years ago Warburg (1908) observed that fertilisation of the sea urchin eggs was followed by a considerable increase in the respiration rate. Whitaker (1933) has demonstrated that if the respiration of the unfertilised egg of marine animals is low, then it rises on fertilisation, while if it is high it falls when the egg is fertilised.

So far we have considered only the internal constitution of a living cell and have said nothing about the factors which control the activity of the large assemblage of enzymes within the cell so that it works as a coordinated whole.

We can say nothing about the internal arrangements which compel the various enzyme systems to work in the right order and each to the extent necessary for the coordinated working of the whole. Some of this control is conditioned by the external environment. In the unicellular organism like an amoeba or a bacterium, the external environment is the fluid surrounding it. Changes in the chemical composition of this fluid, the availability of suitable substrates, the effect of dissolved substances on the osmotic pressure, the surface tension, the hydrogen ion concentration and so on as well as temperature and other purely physical factors all are concerned. Increasing the temperature, raising the concentration of substrates within certain limits increase the activity and the rate of growth of unicellular organisms. Different kinds of unicellular organisms have different complements of enzymes so that the substances produced by enzyme action and excreted from the cell are very different and other activities of the cell are different. In the multicellular organisms the same considerations apply to each individual cell, but here there is an extraordinarily large measure of control of the nature of the environmental fluid. Each cell in the multicellular organism plays its part in this control, besides having its own specific activity. Thus in the higher animals the hydrogen ion concentration of the blood and tissue fluids and the content of many of the dissolved substances are kept remarkably constant and this constancy is essential for the continued coordinated activity of the cell. Destroy this constancy and the enzyme systems within some or all of the cells get out of step.

The introduction of substances normally foreign to the cells into the environmental fluid may also affect some or all of the cells in a variety of ways. Here we have to consider the effects of drugs on cells and their activity.

Certain substances are required in the diet of organisms, whether unicellular or multicellular, in very small quantities only, if the cells are to function properly. Others must be present in the environmental medium in small quantities but are substances which have not entered with the diet but have been produced by certain cells of the multicellular organism. These are the hormones. In a recent article, Green (1941) has developed the thesis that "any substance which occurs in traces within the cell and which is necessary in traces in the diet or medium must either be an essential part of some enzyme system or the enzyme itself. The trace substance-enzyme thesis boils down to the view that enzyme catalysis is the only rational explanation of how a trace of some substance can produce profound biological effects."

Among these substances are the vitamins and hormones. We have seen already that certain of the vitamins form parts of essential enzyme systems.

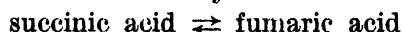
Thus nicotinic acid, the antipellagra vitamin, is a part of the pyridine dinucleotide enzymes, riboflavin is present in several different enzyme systems and so too, is thiamine, vitamin B₁. The relationship of the other vitamins to enzyme systems we do not yet know, but there is some indirect evidence that they play similar parts. It is not unreasonable to consider the vitamin A-protein complex, visual purple, in the retina as part of an enzyme system. Cells vary greatly in their requirements for vitamins from outside. Some free-living cells seem to be able to synthesise every organic substance they require from inorganic materials. For example one of the sulphur bacteria grows on a strictly inorganic medium yet contains thiamine, pyridoxine, biotin, nicotinic acid, pantothenic acid and riboflavin, which it must have synthesised (O'Kane, 1942). Some forms of *proteus vulgaris* require nicotinic acid or one of its derivatives as the sole growth factor—other strains grow well on a simple ammonium lactate medium. *Streptococcus hemolyticus* needs at least thiamin,

nicotinic acid, adenine or related purines, and probably biotin. In the higher multicellular organisms the requirements for different vitamins is in general wider, but even here there are differences. So far as we know at present, ascorbic acid must be provided for only man, the higher apes and the guinea-pig; other animals synthesise what they require.

Hormones are chemical substances produced in one set of cells affecting cell activity in some other part of the organism. They have many parallels with the vitamins. The concentrations at which hormones exert their activity are of the same trace order of magnitude as those of vitamins. The hormones vary greatly in chemical complexity. Some, such as insulin, are highly complex proteins, apparently without any prosthetic group. Others, such as adrenalin, are quite simple chemical substances. Green (1941) suggests that we may consider hormones as either potential enzymes or as prosthetic groups. The protein insulin plays an important part in some phases of carbohydrate metabolism in the animal body. Its action strongly suggests a catalytic action, but whether insulin can itself act as an enzyme or can form a part of an enzyme system, we do not know. Thyroxin occurs in the body in combination with protein-thyreoglobulin, and as such it leaves the thyroid gland. Thyroxine in some way controls the metabolic level of animal cells and it is not improbable that, in combination with some other protein within the cells, it acts as an enzyme or part of an enzyme system. Such simple hormones as adrenalin and the sex hormones might act as prosthetic groups of enzyme systems, in the case of adrenalin probably of short-lived duration.

Certain drugs affect cells by interfering with enzymic activity, either by competing with the normal substrate of some enzyme system or by competing with the normal prosthetic group of some enzyme producing a pseudoenzyme which is inactive, or by combining with the enzyme and rendering it inactive.

Malonic acid can compete with succinic acid as substrate for the enzymic system present in most cells which catalyses the reaction



but is itself not attacked by the enzyme.

Para-amino benzoic acid is essential for the metabolism of many cells or rather for the metabolism associated with reproduction. Some cells can synthesise it themselves, but others cannot, and it must be supplied from outside. Bacteria which cannot make it have their growth stopped by the closely related sulphanilamide (Figure IV), but it requires about 5,000 times as much sulphanilamide as the coincident p-amino benzoic acid to inhibit growth of streptococci *in vitro*. It is believed that the action is competitive, the p-amino-benzoic acid being either an essential metabolite for certain cell processes or more likely a part of some enzyme system. Sulphanilamide does not affect the normal oxidising systems of cells.

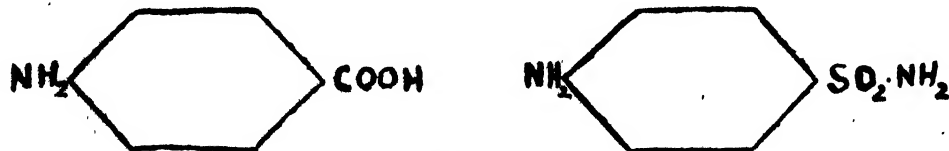


Fig. IV.

The idea that competition may occur between closely related substances had led to the study of substances related to parts of known prosthetic groups such as nicotinic acid, and to other essential growth factors which probably play a part in enzyme action such as pantothenic acid. Thus pyridine-3-sulphonic acid can inhibit bacterial growth by competing with nicotinic acid

(McIlvain, 1940), the sulphonic analogue of pantothenic acid competes with pantothenic acid (Snell, 1941).

Some substances can combine with a particular part of an enzyme system and so put it out of action. For example, cyanides poison cells by combining with some component of the cytochrome system and so putting out of action the main path of oxidation in aerobic cells. There may be, and probably always are, several paths of oxidation in cells, but one of them, generally that connected with the cytochrome system, accounts for the predominant part of the oxidation. Yeast cells are very sensitive to cyanides, but Stier and Castor (1941) have developed a substrain of yeast by culturing in a medium containing cyanide which lacks cytochrome oxidase. Here there must have developed a considerable alteration in the enzyme systems of the yeast cells.

Surface-active substances have marked effects on cells in many cases leading to death as in those which act as powerful bactericidal agents, in other cases interfering with cell activity to a less extent. Surface-active substances are effective protein denaturing agents and can dissociate conjugated proteins. In some cases the action of the surface-active substance may be removed by washing away the substance, so the change in the proteins cannot be great.

Michaelis and Quastel (1941) have brought forward evidence that the narcotics, which form an extremely varied chemical group and are surface-active substances, produce their action by combining in some way with some flavo-protein or some component of the tissue respiratory system between flavo-protein and cytochrome oxidase.

Some drugs appear to act by inhibiting enzyme systems in cells and, by providing unused substrate, apparently stimulate other enzyme systems. An example of this is dinitrophenol. This greatly stimulates oxygen uptake by certain bacteria and yeasts and also animal cells, but causes inhibition of cell growth. It appears that, by blocking some of the synthetic reactions, it allows complete oxidation of substrate.

Many other examples could be given of the effects of drugs on cell enzyme systems, but sufficient has been said to indicate that this aspect is an important one, if not the most important one, in the action of drugs.

Even with the limitations of existing knowledge, to develop the thesis which I have advanced fully would take a considerable time and I have had to make a selection of available evidence. I hope, however, that I have been able to make a good case for the idea the life of a cell is dependent on, and is inherent in, the enzymes contained in the cell and the organisation within the cell of these enzymes.

I shall conclude with a quotation from Claude Bernard, the father of modern experimental physiology, on the subject of scientific theories: "they are only partial and provisional truths which are necessary to us, as steps upon which we rest, so as to go on with investigation; they embody only the present state of knowledge and consequently they must change with the growth of science".

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NOVA PUPPIS 1942.

By H. W. WOOD.

Manuscript received, February 13, 1943. Read (in title only), April 7, 1943.

The announcement of the discovery of this Nova, in which it was stated to be blue in colour, first magnitude and still brightening, was passed on to us by Dr. J. M. Baldwin, Government Astronomer for Victoria, on November 13, 1942. When the Nova was seen here that evening at 11h. 30m. U.T. it was distinctly reddish and was noted to be a little brighter than ϵ Canis Majoris ($m=1.63$). The red colour seemed to show that the emission lines had begun to dominate the spectrum, the red being due to $H\alpha$ (e.g. Payne-Gaposchkin and Gaposchkin, 1938) and this, together with the failure of the magnitude to increase, seemed to indicate that maximum had passed. This note records some observations made at intervals during a period of frequently cloudy weather.

Transit observations (with fundamental stars on the FK3 system) were made of the star's position on five occasions with the result

R.A. 8h. 7m. 58s.33 Dec. $-35^{\circ} 3' 8''.7$ (1900.0)

This corresponds to galactic longitude $220^{\circ}.6$ and latitude $+0^{\circ}.1$ with the position (1900.0) of the galactic pole R.A. 12h. 40m., Dec. $+28^{\circ}$, so that the star conforms to the well-known tendency of novæ towards galactic concentration.

Using this position, available sources were examined to find if possible a record of the star before its outburst. The place which it would occupy in the Perth Astrographic Catalogue was computed, but the star was not recorded. Neither was it recorded in the "Harvard Sky" plates or our copy of the Franklin Adams Chart. This sets a limit to its brightness at various epochs as in Table 1.

TABLE 1.

Date of Plate.	Mag. Limit.	Chart.	Justification for Limiting Mag.
1903, May 6	11½	<div> <div>"Harvard Sky" } "Harvard Sky" } Franklin Adams Chart. Perth Astrographic Catalogue } Perth Astrographic Catalogue } Union Observatory Chart.</div> </div>	1
1903, December 23	11½		
1912, April 19	16		2 and 3
1913, February 28	13		
1914, April 15	13		4
1927, February 6	14		

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The Union Observatory Chart shows, in the vicinity of the Nova, a number of stars intermediate between that of the Perth Astrographic Catalogue and the Franklin Adams Chart, so that 14 would probably be a fair estimate of its

whereby, for example, c 3 e means a magnitude three-tenths of the way from c to e. Comparisons, made by naked eye till November 18 and thereafter with a two-inch telescope, were sometimes not easy because of the differences in colour among the stars, the Nova being distinctly reddish. Some observations by W. H. Robertson are included at the end of the table. Since January 6 only stars selected by Father D. J. O'Connell, Director of Riverview College Observatory, for use by the Variable Star Section of the N.S.W. Branch of the British Astronomical Association, have been used. The star H.D. 67736 may be variable. Its magnitude according to Harvard photometric observations (Harvard Annals 1895 and 1901) is 7.36, but the residuals are slightly large and to me it has appeared (January 6 to January 17) brighter than either p or q. The rapidity of the magnitude development of the Nova seems to place it in the "flashing" type of Gerasimovic (1936); by December 14 it had fallen through five magnitudes but since then has been fairly constant.

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A POLYHEDRAL MODEL OF THE PROJECTIVE PLANE.

By F. A. BEHREND.

Communicated by Professor H. S. CARSLAW.

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The first satisfactory topological model of the projective plane in 3-space was described by Boy¹ (1901): a bounded surface which crosses itself along a certain curve but otherwise is everywhere regular. The problem of an algebraic, or even only an analytic, representation of Boy's surface is still unsolved. Recently Merz² (1942) and Humbert³ (1942) obtained polyhedral varieties of Boy's surface. Merz's surface has 16 faces, 18 vertices and 33 edges; Humbert's has 16 faces, 24 vertices and 39 edges.

In the present paper a model is described which appears⁴ to be of a much simpler type; it has 10 faces, 12 vertices and 21 edges; it is likely that it is the simplest polyhedron of this kind.⁵

The surface is obtained as follows: it possesses the line $x_1 = x_2 = x_3$ as an axis of order 3; there are four vertices in each coordinate plane; those in the plane $x_1 = 0$ are conveniently chosen as

$$P_1 = (0, 0, 2), Q_1 = (0, -3, -1), R_1 = (0, 1, -1), S_1 = (0, 1, 1),$$

and the others are obtained by cyclic permutation:

$$P_2 = (2, 0, 0), Q_2 = (-1, 0, -3), R_2 = (-1, 0, 1), S_2 = (1, 0, 1),$$

$$P_3 = (0, 2, 0), Q_3 = (-3, -1, 0), R_3 = (1, -1, 0), S_3 = (1, 1, 0).$$

The three (congruent) quadrangles $P_i Q_i R_i S_i$ ($i=1, 2, 3$) (Fig. 1a) form three faces of the polyhedron lying in the coordinate planes and crossing each other along segments $A_k B_k$ of the coordinate axes where A_k, B_k are the unit points on the x_k axis ($x_j = 0$ for $j \neq k$, $x_j = \pm 1$ for $j = k$) (Fig. 2a). The three (congruent) quadrangles $P_1 Q_1 R_3 S_2$, $P_2 Q_2 R_1 S_3$, $P_3 Q_3 R_2 S_1$ (Fig. 1b) form another triplet of faces (Fig. 2b; it is seen that P_1, Q_1, R_3, S_2 lie in the plane $x_1 - x_2 + x_3 - 2 = 0$, etc.). Again, $Q_1 R_1 S_3 R_3$, $Q_2 R_2 S_1 R_1$, $Q_3 R_3 S_2 R_2$ (Fig. 1c) form a triplet of faces (Fig. 2c; Q_1, R_1, S_3, R_3 are in the plane $x_1 - x_3 - 1 = 0$); they intersect the coordinate planes, i.e. the first three faces, along $A_1 B_3$, $A_2 B_1$, $A_3 B_2$. All nine faces are shown in Fig. 2d; the polyhedron is now closed by a last face, the hexagon $S_1 P_1 S_2 P_2 S_3 P_3$ (in the plane $x_1 + x_2 + x_3 - 2 = 0$, Fig. 1d) which actually coincides with the regular triangle $P_1 P_2 P_3$, the S_i being the midpoints of its sides.

¹ See Hilbert and Cohn-Vossen, *Anschauliche Geometrie*, Springer, Berlin, 1932, pp. 266-283.

² Einseitige Polyeder nach Boy. I. Einseitiges Hexadekaeder, *Comment. Math. Helv.*, 14, 1942, pp. 134-137.

³ Einseitige Polyeder nach Boy. II. Polyèdre sans singularités topologiques homéomorphe au plan projectif dans l'espace à 3 dimensions, *ibid.* pp. 137-140.

⁴ The original papers of Merz and Humbert were not available to the author; a review is found in *Mathematical Reviews*, 3, 1942, p. 299.

⁵ As Boy's surface possesses an axis of order 3, the possible models will probably have $3k+1$ faces; the one-sided heptahedron (viz. *loc. cit.* 1) has six singularities; the next possible case is the dodekahedron.

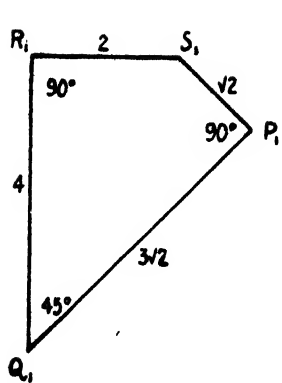


Fig. 1a.

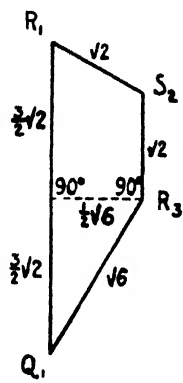


Fig. 1b.

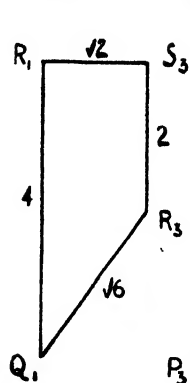


Fig. 1c.

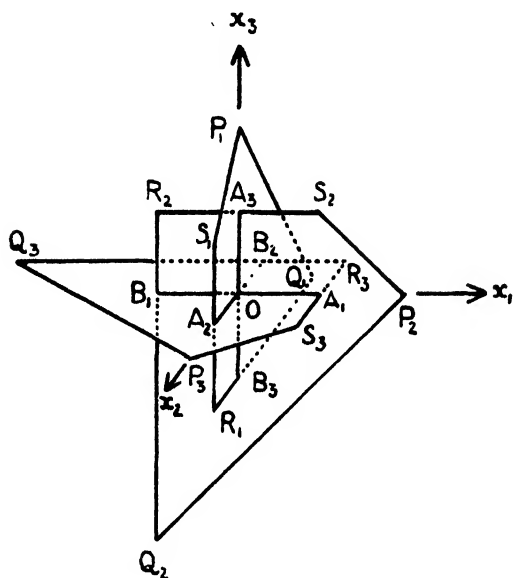
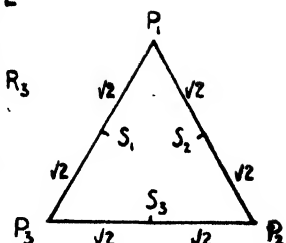


Fig. 2a.

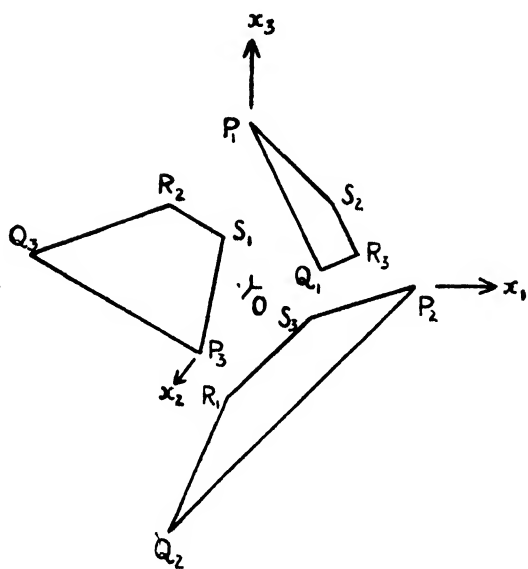


Fig. 2b.

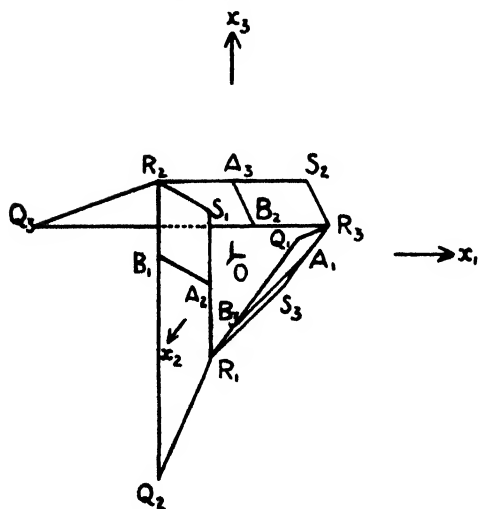


Fig. 2c.

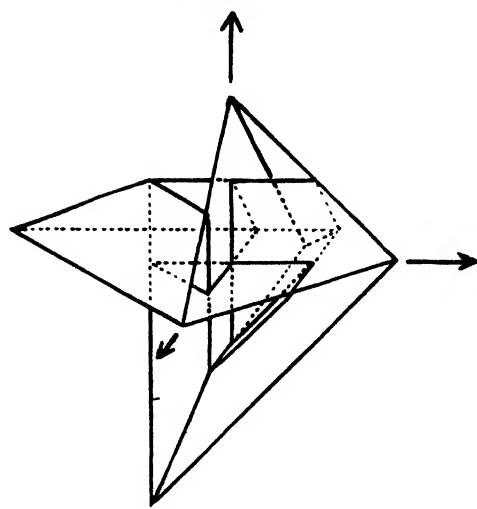


Fig. 2d.

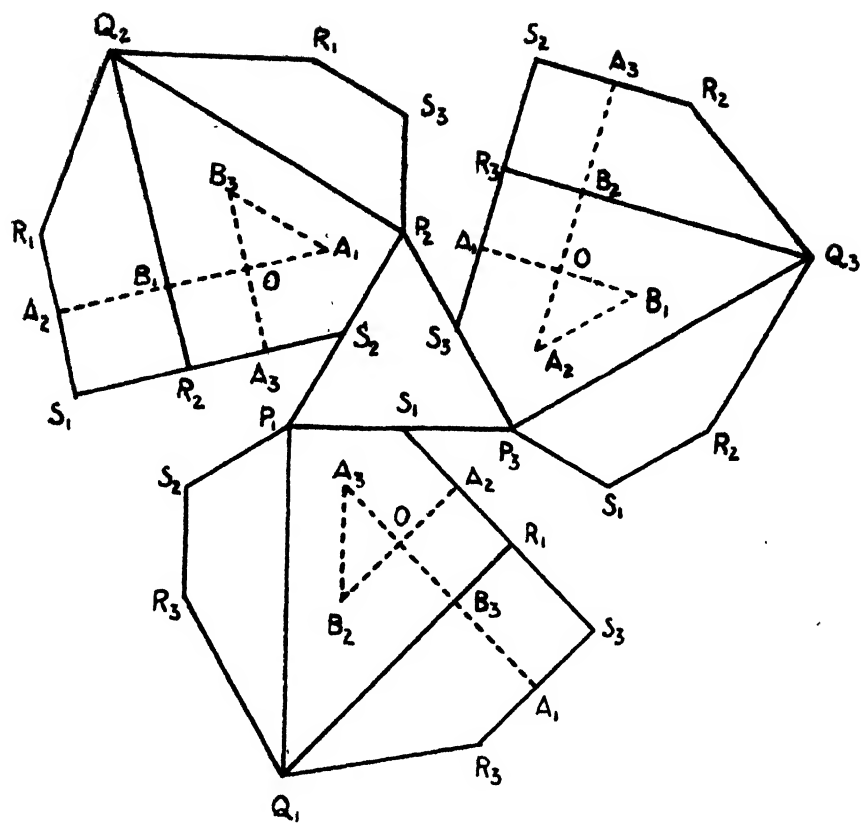


Fig. 3a.

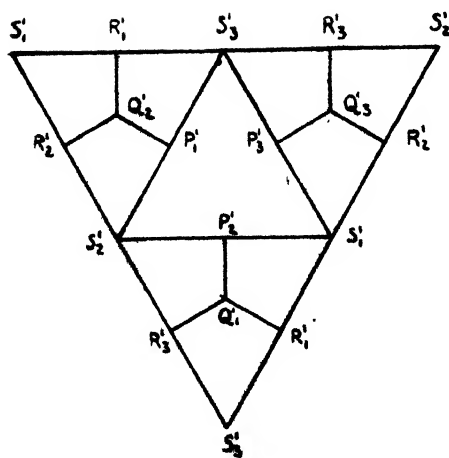


Fig. 3b.

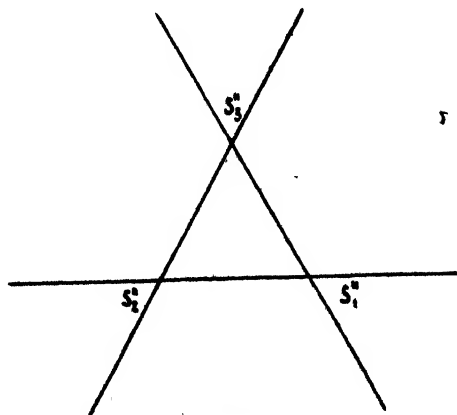


Fig. 3c.

That the polyhedron thus constructed is a model of the projective plane is easily seen. Its net is shown in Fig. 3*a*. It is topologically equivalent to the triangle $S'_1S'_2S'_3$ of Fig. 3*b*, "diametral" points of whose boundary have to be identified, and this triangle, in turn, is topologically equivalent to the complete projective plane (Fig. 3*c*). The mapping can easily be studied in detail.

A paper model can readily be constructed from the net which has to be cut along the lines A_1B_1 , B_1A_2 in the quadrangle $P_3Q_3R_3S_3$ and the corresponding lines obtained by cyclic permutation. The model may actually be folded from a single piece passing the edges $S_2R_2S_1$, $S_3R_3S_2$, $S_1R_1S_3$ simultaneously through the cuts $A_1B_1A_2$, $A_2B_2A_3$, $A_3B_3A_1$, but it may be found more convenient to detach the triangle $P_1P_2P_3$ and to use four separate pieces.

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February, 1943.

PRELIMINARY NOTES ON SOLUTION-CRACKING TREATMENT OF TORBANITE.

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INTRODUCTION.

The organic matter of torbanite, when subjected to the usual method of retorting, first undergoes a change to a semi-solid material, or intermediate-product, which decomposes at higher temperatures into gas, oil vapour and carbon (Cane, 1942). The liquid products of this decomposition constitute a crude oil, which is used as a cracking stock for conversion to petrol. The original organic matter of torbanite is insoluble in organic solvents; but the intermediate-product, formed by heat, is soluble, and can be extracted with common solvents (Cane, 1942; Dulhunty, 1942*a*, 1942*b*; Diakova and Stepantzeva, 1940). This property makes possible a *solvent extraction* process in which the torbanite is first preheated and then extracted with solvents; but the extracted products, when separated from the solvent, are of the nature of a heavy, black oil, which must be subjected to further treatment—such as cracking or hydrogenation—to convert it to petrol. Preheating and extraction may be carried out in one operation by using a solvent with a critical temperature higher than that required to render the organic matter soluble. Torbanite crude oil, obtained either by retorting or solvent extraction, can be used as the solvent at the required temperature. It undergoes cracking, however, but the solvent oil is replaced by oils extracted from the torbanite, and the products of cracking represent the final products desirable in the treatment of torbanite. This method of treatment, in which preheating, extraction and conversion of heavy oil to light products are effected simultaneously, may be referred to as solution-cracking; and experiments in its manipulation are described here.

SOLUTION-CRACKING TREATMENT.

Experimental Conditions.

The conditions involved in solution-cracking include three variable factors—temperature, pressure and time. The temperature must be sufficient to convert the organic matter to the soluble intermediate-product, and at the same time to crack the extracted products as well as the solvent oil. The purpose of pressure is to keep sufficient of the solvent oil in the liquid phase to effect the solution of the intermediate-product, and, also, to keep the heavier cracked products, such as oil boiling from 200° C. to 300° C., in a suitable phase condition to enable them to be cracked to petrol. The extraction time depends on the extraction temperature for any particular solvent oil, but must be sufficient to effect the complete, or almost complete, conversion of the organic matter to the soluble intermediate-product.

The main control problem, in connection with the conditions of operation, is the balancing of the amount of cracking and the rate of extraction. If the cracking is excessive during the time necessary to complete the extraction, the volume of the oil stock will decrease with successive extractions, and must be

replaced from external sources. If the cracking is insufficient, the volume of the oil stock will increase, or stocks of heavy, cracked products will be built up.

The extraction temperature determines both the amount of cracking and the rate of extraction; but evidence obtained from experimental work suggests that, with increasing temperature, the amount of cracking increases more rapidly than the rate of extraction, giving a limiting temperature of operation above which the volume of the oil stock will decrease. This is due, no doubt, to the fact that the lighter cracked products, which are more refractory, crack very slowly at the lower temperatures, below $400^{\circ}\text{C}.$, and tend to maintain the volume of the oil stock, but above $400^{\circ}\text{C}.$ they commence to crack at appreciable rates, and rapidly increase the total amount of cracking.

Solution-cracking, in laboratory equipment, has been accomplished by two methods. (i) By heating the solvent oil and the torbanite for short periods of time under the pressure of the vapours in the system at the temperature of the extraction, and removing the light products (petrol or light fuel oil, as required) by distillation between each heating stage. This method would be equivalent to recycling the reaction mixture several times through a heating unit, and removing the light products by flashing, or pressure-distillation, between each cycle. (ii) By heating for the full extraction time in one stage, and constantly removing the vapours of light products by releasing excess gas so as to maintain a constant pressure on the system. This method would approximate to passing the oil and torbanite through a heating unit, and then allowing the mixture to remain in a reaction chamber, at a given temperature and pressure for the required length of time to complete the extraction.

The influence of pressure, in relation to the extraction temperature, is particularly important in the second method, as it directly determines the removal of certain products from the reaction almost as soon as they are formed. The fractions possessing a critical temperature (under the existing conditions) lower than the extraction temperature, will be removed at any pressure, but those with higher critical temperatures will be allowed to remain in the reaction zone until their constitution is such that their vapour-pressures, under the conditions of the multiple component system, become equal to the pressure which is maintained. The pressure required to allow the removal of certain light products, such as petrol, and keep the heavier fractions in the reaction zone, depends on the phase equilibrium existing in the reaction mixture, and this is a function of the concentration on the various components, as well as temperature. Consequently the actual pressure required at a given extraction temperature departs widely from calculated figures based on the critical temperatures of hydrocarbons of various boiling points.

In the following experiments, involving the continuous removal of gas and light products, a pressure was maintained, which would give a pressure distillate of the required specific gravity. The relation between temperature and the required pressure tends to vary during the extraction owing to the changing concentration of the components in the system. In an extraction carried out at a constant temperature of $380^{\circ}\text{C}.$, the required pressure may vary from 180 to 225 lb. as the extraction proceeds, and the concentration of heavy products decreases owing to cracking. In extractions in which the temperature is gradually increased from $350^{\circ}\text{C}.$ to $400^{\circ}\text{C}.$, during the extraction, the required pressure may vary from 125 lb. at the commencement of the extraction to 300 lb. at its conclusion, owing to the fact that both temperature, and the proportion of light components, increase as the extraction proceeds.

EXPERIMENTAL DATA AND RESULTS.

Early experiments in solution-cracking were based on the principle of heating the torbanite and solvent oil for short periods of time, or recycling, until

the extraction was complete, and, between each cycle, removing low-boiling products by distillation under atmospheric pressure. The number of cycles required to complete the extraction depended on the temperature and time for each cycle. Relatively low temperatures were used for the first cycles of each extraction, as most of the heavy, liquid intermediate-product is then being cracked, and low temperatures effect this cracking more efficiently. Higher temperatures were used in the later stages. The pressure was allowed to increase during each cycle as gaseous and light, liquid hydrocarbons were formed.

It was found that large numbers of cycles of short duration, involving low operating pressures, tend to produce high yields of liquid products and small volumes of gas, due to a minimum amount of cracking. The liquid products, however, contain relatively large quantities of heavy fractions, and may be expected to possess low anti-knock properties. Smaller numbers of cycles of longer duration, involving higher pressure, give greater volumes of gas; but the liquid products contain larger proportions of light fractions, and would be expected to possess higher anti-knock properties. The following experiments, Nos. 1 and 2, illustrate the method adopted in carrying out multiple-cycle solution-cracking.

Later work was based on the continuous removal of gas and light products during the solution-cracking process, thus effecting complete extraction in one operation, and eliminating the necessity for recycling. In this method, illustrated by experiments Nos. 3, 4, 5 and 6, the time required to complete each extraction is determined by the temperature of operation, and a pressure is maintained on the system sufficient to allow light products, of required boiling range, to be removed as vapour with the gaseous hydrocarbons. The amount of cracking which occurs during the extraction is governed by both temperature and pressure. Preliminary experiments show that low temperatures and pressures, requiring long extraction times, give small volumes of gas and large yields of relatively low-quality liquid products. Higher temperatures and pressures involving short extraction times produce greater volumes of gas and somewhat smaller yields of better-quality liquid products.

EXPERIMENTAL.

Multiple-cycle Solution-cracking.

Experiment No. 1.

The apparatus consisted of a 2 l., cylindrical, high-pressure vessel, approximately 16.5 by 3.5 in. (see Dulhenty, 1942*a*), completely closed except for a fine tube leading to a needle valve and pressure gauge. The body of the vessel was enclosed in, and heated by, an electric muffle. Temperatures were recorded by means of a thermocouple located in a sheath which projected into the cylinder.

One pound of Coolaway Mountain torbanite (see Table 5), crushed to pass a $\frac{1}{2}$ in. screen, was mixed with 1 l. of torbanite-crude oil distillate (B.P. 230°–250° C.) and placed in the pressure vessel. The mixture was subjected to successive heating-cycles until the volatile content of the solid residue was reduced to approximately 15%. This required seven cycles under the temperature-pressure-time conditions for each cycle, given in Table 1.

TABLE 1.

Conditions in Experiment No. 1 on Multiple-cycle Solution-cracking.

Cycle No.	1	2	3	4	5	6	7
Temperature, ° C.	375	390	400	400	400	400	400
Time, min.	15	15	15	15	20	30	60
Max. pressure, lb. sq. in.	126	140	154	150	190	200	230

After each cycle the vessel was cooled to 240° C. and kept at that temperature while gas and vapours of light products were released through a condenser. The gas was measured, and the condensate fractionated into petrol (below 180° C.), light oil (180–230° C.) and residue (above 230° C.), which was returned to the pressure vessel. When the extraction was complete, the solid residue was filtered from the solvent oil stock and washed with benzene to remove the last of the oil. The oil was recovered from the benzene by heating in a distilling flask at 200° C. and then added to the solvent oil stock. This was made up to 1 l. with the original, heavy distillate, and used as the solvent oil for the next extraction. Three solution-cracking treatments were carried out in this way, the average results being set out in Table 2.

TABLE 2.
Average Results in Experiment No. 1 on Multiple-cycle Solution-cracking.

Cycle No. ..	1	2	3	4	5	6	7	Total.
Gas, l.	0.44	1.71	2.5	1.5	2.5	2.7	3.8	15.15
Petrol below 180° C., ml. . .	7	11	10	16	24	30	38	135
Light oil, 180°–230° C., ml. . .	75	90	30	50	43	74	89	451
Final oil stock								870 ml.
Total net yield of light products								456 ml. or 224 galls per ton
Yield of gas								957 cu. ft. per ton
Percentage by wt. conversion of organic matter to light products								84%
Fraction of light products distilling below 180° C.								30%
Fraction of petrol products distilling below 100° C.								25%
Sp. gr. of petrol (below 180° C.)								0.74
Sp. gr. of light oil (180°–230° C.)								0.83
Sp. gr. of final oil stock								0.91

Experiment No. 2.

The apparatus was similar to that used for Experiment No. 1. One pound of Coolaway Mountain torbanite (see Table 5), crushed to pass a $\frac{1}{4}$ in. screen, was mixed with 1 l. of torbanite-crude oil distillate (200°–220° C.) and subjected to three heating-cycles under the temperature-pressure-time conditions given in Table 3.

TABLE 3.
Conditions in Experiment No. 2 on Multiple-cycle Solution-cracking.

Cycle	1	2	3
Temperature, ° C.	375	390	400
Max. pressure, lb. sq. in.	546	476	406
Time, min.	60	90	120

After each cycle, gas and spirit vapour were removed by distillation from the vessel under atmospheric pressure and at 200° C. The crude condensate was fractionated into petrol (below 180° C.) and residue, the latter being returned to the pressure vessel. After the completion of the third cycle (the volatile content of the residue being reduced to 14%), and the removal of light products, the

contents of the vessel were removed, and the solid residue separated from the final oil stock by filtration and washing with benzene as described in Experiment No. 1. The oil stock, which amounted to approximately 1 l., was mixed with 1 lb. of fresh torbanite, and the next solution-cracking treatment carried out as before. Ten batches of 1 lb. each were treated in this way. The volume of the solvent oil stock remained constant—no additional solvent oil being used. The average yields of gas and petrol, obtained from each cycle, and the totals for each batch are summarised in Table 4.

TABLE 4.

Average Results in Experiment No. 2 on Multiple-cycle Solution-cracking.

Cycle	1	2	3	Total.
Gas, l.	15	10	6	31
Petrol (below 180° C.), ml. . .	82	80	76	239

Final oil stock	1 l.
Yield of gas	2,453 cu. ft. per ton
Total net gain in petrol	120 galls. per ton
Percentage by wt. conversion of organic matter to petrol	40
Sp. gr. of petrol	0.73
Sp. gr. of oil stock	0.87
Fraction of petrol distilling below 100° C.	35%

SOLUTION-CRACKING BY CONTINUOUS REMOVAL OF PRODUCTS.

Experiment No. 3.

The apparatus consisted of the pressure vessel already described, and used in Experiments Nos. 1 and 2. A condensing system was connected in place of the gauge, on the high-pressure side of the needle valve. The condenser, in direct communication with the cylinder of the pressure vessel, carried a pressure gauge and separate valves for drawing off condensate and releasing excess gas; thus providing for the condensation of vapours under pressure.

A series of five solution-cracking treatments was commenced with 1.5 lb. of selected Glen Davis torbanite (see Table 5), crushed to pass a $\frac{1}{4}$ in. screen, and 900 ml. of heavy oil (boiling above 250° C.) previously extracted from torbanite.

TABLE 5.

Torbanite Samples used in Experimental Work on Solution-cracking.

Experiment Number.	Origin of Sample.	Proximate Analyses.			Ash.	Gray King Assay. Galls. per ton.
		Hygro. Moist.	Vol. Cont.	Fixed Carbon.		
1, 2, 5, 6	Coolaway Mt. run of mine	0.08	79.02	17.05	3.85	105
3	Glen Davis selected sample	0.25	66.45	11.60	21.70	141
4	Glen Davis run of mine	1.50	48.5	14.4	35.6	102

The temperature was raised rapidly to 360° C., then, slowly, over a period of 4 hr., to 400° C. This was sufficient to complete the extraction. The pressure, controlled by releasing gas from the condensing system, was gradually increased with the temperature from 125 lb. sq. in. at 360° C. to 220 lb. sq. in. at 400° C. After the 4-hr. heating period, the vessel was cooled, the contents removed and the solid residue separated from the solvent oil stock by filtration and washing with benzene (see Experiment No. 1). The pressure distillate, obtained during the treatment, was fractionated into petrol (below 180° C.) and residue, the latter being returned to the solvent oil stock. Each of the four following treatments involved the use of 1.5 lb. of torbanite, and the solvent oil stock from the previous batch. The yields of gas and petrol and the conditions of treatment are summarised in Table 6.

Experiments Nos. 4, 5 and 6.

The apparatus, general technique and weights of torbanite employed in these experiments were the same as in Experiment No. 3. The torbanite, used in Experiment No. 4, was an average sample from the Glen Davis deposit (see Table 5), and the solvent stock (750 ml.) was smaller than in Experiment No. 3, as the torbanite, under treatment, was of somewhat lower quality. Experiment No. 5 was made on Coolaway Mountain torbanite (see Table 5), using 1,000 ml. of solvent oil stock, and the solution-cracking was effected under constant temperature-pressure conditions—400° C. and 250 lb. sq. in., respectively. In Experiment No. 6, the sample of torbanite and volume of solvent oil stock were similar to Experiment No. 5; but the temperature and pressure were gradually increased from 100 lb. sq. in. at 350° C. to 200 lb. sq. in. at 400° C. over a period of 5 hr. The experimental conditions and yields of products for Experiments Nos. 4, 5 and 6 are summarised in Table 6.

TABLE 6.

Conditions and Yields in Experiments Nos. 3, 4, 5 and 6 on Solution-cracking with Continuous Removal of Products.

Exp. No. and Sample.	Sol. Oil Stock, ml.	Weight of Torb. lb.	Temp.-press.-time Conditions.			Total Gas. Cu. ft. per ton.	Petrol. Galls. per ton.	Theor. Max. Yield Petrol. Galls. per ton.
			t° C.	Hr.	Lb. sq. in.			
3. Selected Glen Davis.	900	1.5	Increase 360-400	4	Increase 125-220	3,826	89	101
4. Glen Davis run of mine.	750	1.5	Increase 360-400	4	Increase 125-220	3,189	74	84
5. Coolaway run of mine.	1,000	1.5	400	2.5	250	4,464	100	125
6. Coolaway run of mine.	1,000	1.5	Increase 350-400	5	Increase 100-200	3,900	115	125

SOLUTION-CRACKING IN ONE CYCLE WITHOUT THE REMOVAL OF PRODUCTS.

Experiment No. 7.

This experiment was made with the object of obtaining data relating to the special conditions of cracking and pressure, which obtain when solution cracking is carried out in one cycle without the removal of products.

The apparatus consisted of the high-pressure vessel, as used in Experiments Nos. 1 and 2, completely closed except for the fine tube leading to a high-pressure gauge and the closed needle valve. One pound of Coolaway Mountain torbanite, crushed to pass a $\frac{1}{4}$ in. screen, was mixed with 1 l. of solvent oil stock (boiling above 250°C .), and heated in the closed vessel at a temperature of 390°C . for a period of 6 hr. No products were withdrawn during the treatment; thus the pressure was allowed to build up as a function of the gas and light, liquid products formed during the total period. The high pressures, which existed during the latter stages of the treatment, probably kept all hydrocarbons with critical temperatures above 390°C . (under the existing conditions) in the liquid phase, and so allow extensive cracking of some of the light products. It is also probable that some polymerisation of the gaseous hydrocarbons may have resulted from the high pressures. The rate of increase of pressure with time, and the yields and nature of the products are summarised in Table 7.

TABLE 7.

Time-Pressure Relations and Products Obtained in Experiment No. 7 on Solution-cracking in One Cycle without Removal of Products.

Time at 390°C . hr.	Pressure, lb. sq. in.	Pressure Increment each $\frac{1}{4}$ hr. lb. sq. in.	Continued.			Continued.		
			Time.	Press.	Inc'nt.	Time.	Press.	Inc'nt.
—	200	—	$2\frac{1}{4}$	1,628	108	$4\frac{1}{4}$	2,228	62
$\frac{1}{4}$	295	95	$2\frac{1}{2}$	1,722	94	$4\frac{1}{2}$	2,289	61
$\frac{1}{2}$	400	105	$2\frac{3}{4}$	1,799	77	5	2,352	63
$\frac{3}{4}$	598	198	3	1,855	56	$5\frac{1}{4}$	2,420	68
1	803	205	$3\frac{1}{4}$	1,916	61	$5\frac{1}{2}$	2,489	69
$1\frac{1}{4}$	1,013	210	$3\frac{1}{2}$	1,976	60	$5\frac{3}{4}$	2,558	69
$1\frac{1}{2}$	1,228	215	$3\frac{3}{4}$	2,038	62	6	2,623	65
$1\frac{3}{4}$	1,400	172	4	2,101	63			
2	1,520	120	$4\frac{1}{4}$	2,166	65			

Final stock	650 ml.
Yield of petrol (below 180°C .)	230 ml.
Yield of light oil (180° – 230°C .)	225 ml.
Yield of gas	80.5 l.
Net yield of petrol	105 ml., i.e. 53 galls. per ton.
Fraction of light products distilling below 180°C	51%
Fraction of petrol distilling below 100°C	48%
Specific gravity of petrol	0.71
Specific gravity of light oil	0.81
Specific gravity of oil stock	0.86

SUMMARY OF EXPERIMENTAL RESULTS.

The results of Experiment No. 1 illustrate the remarkably high yields of spirit and light oil obtainable, without respect to quality, by multiple-cycle solution-cracking under comparatively low temperature-pressure conditions. The yield of 224 galls. per ton, representing light products formed from the torbanite, is equivalent to a conversion of 84% by weight of the organic matter. The amount of cracking occurring under these conditions is small, giving yields equivalent to 4 cu. ft. of gas per gall. of the total light products formed, and about 957 cu. ft. from the conversion of each ton of torbanite. The quantity of petrol (below 180°C .) represents only 30% of the light products boiling below 230°C .

The specific gravity of the petrol (0.74) is relatively high, only 25% distilling over below 100° C.

Solution-cracking in three cycles (Experiment No. 2) results in additional cracking, which produces a petrol with a specific gravity of 0.73 (35% distilling below 100° C.) and gives a net yield of 120 galls. per ton, although the gas yield is low at about 20 cu. ft. per gallon. It is interesting to compare these results with those obtained in Experiment No. 7, in which the treatment was effected in one cycle without removal of products. This gave more extensive cracking, and produced a petrol with a specific gravity of 0.71 (48% distilling below 100° C.), representing a net yield of only 53 galls. per ton. The gas yield in this case was 55 cu. ft. per gall. of petrol formed.

The results of Experiments Nos. 3, 4, 5 and 6 show that good yields of petrol can be obtained by solution-cracking with continuous removal of products. The gas yields are somewhat higher than those obtained in solution-cracking by recycling, being in the vicinity of 40 cu. ft. per gall. of petrol formed. The petrol, obtained from experiments on the continuous removal of products during solution-cracking of Coolaway Mountain torbanite, possessed the following properties :

Crude petrol :

Specific gravity	0.725
Fraction distilling below 100° C.	35%
Sulphur (Lamp Method)	0.28%
Unsaturated hydrocarbons	21.35%
Aromatic hydrocarbons	18.12%

Petrol refined by light alkali and acid wash (1.5% of 80% H_2SO_4) :

Sulphur	0.26%
Unsaturated hydrocarbons	17.35%
Aromatic hydrocarbons	16.00%

Colour : approximately water-white, colour stable.

"Sweet" to plumbite.

Octane number	58
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The conversion of the organic matter in the torbanite to petrol by solution-cracking is effected without distilling the heavy oils or allowing them to pass appreciably to the vapour phase until they have been cracked to the required final product. The oils, still heavier than the final products at the conclusion of a batch-treatment (i.e. the final oil stock), are used as the solvent oil for the next batch, where they are cracked again. The physical properties of the oil stock depend on the total amount of cracking involved in the treatment, but under given temperature-pressure-time conditions, the boiling range, specific gravity and viscosity of the oil stock remain reasonably constant, after equilibrium has been reached, during a series of batch-treatments. The oil stock is not black and opaque, as may be expected of a liquid residue from cracking as well as extraction, but it is dark-red and somewhat translucent with a strong, light-green fluorescence. This appears to be due to the absence of true coking at the relatively low operating temperatures, and the deposition of any polymerisation products with the carbon formed by cracking. The green fluorescence would appear to be indicative of the presence of considerable quantities of paraffin hydrocarbons.

The particle size of the torbanite (up to 1 in. cubes and possibly larger) does not influence the rate or efficiency of extraction (Dulhunty, 1942b). The solid residues, from the foregoing solution-cracking experiments, were fine, black powders together with some hard carbon deposited on the walls of the reaction vessel. These residues consisted of the inorganic material and small amounts of

vascular plant debris (humosite) originally present in the torbanite, together with carbon formed by cracking. The proximate compositions of the fresh torbanite and residue, after treatment in Experiment No. 2, are as follows:

Fresh torbanite: Volatiles, 79.10%; fixed carbon, 17.05%; ash, 3.85%.

Residue: Volatiles, 14%; fixed carbon, 70%; ash, 16%.

The pressure vessel used for experimental work on solvent extraction and solution-cracking treatment of torbanite was constructed entirely of mild steel. No evidence of corrosion was found on the inner surfaces on the cylinder and needle valve after the vessel had been used for a total running time of approximately 600 hr. Hard carbon was removed from the walls and base of the cylinder; and the surface of the steel, although dull, still carried the fine striæ from the machining of the vessel when it was made. There was no pitting, and the dull surface was made bright by light rubbing with fine emery paper. The thermocouple sheath, projecting into the cylinder to a central position, carried a light coat of soft carbon, which was removed by scraping with a piece of wood. This exposed bright steel showing the fine striæ from the original turning of the sheath. The parts of the needle valve were examined, but no evidence of corrosion was found. Thus it was concluded that no appreciable corrosion of mild steel occurs during solution-cracking at temperatures in the vicinity of 400° C. On one occasion a copper strip, $\frac{1}{2}$ in. in thickness, was placed in the vessel. After 16 hr. running, at temperatures between 350° and 400° C., much of the copper was changed to copper sulphide, and holes appeared in the strip, indicating vulnerability of copper to the action of sulphur compounds during solution-cracking.

ACKNOWLEDGMENTS.

The investigations outlined in this paper were made possible by a Commonwealth Research Fellowship, and the purchase of equipment by assistance from the Commonwealth Research Grant to the University of Sydney.

The writer wishes to acknowledge valuable discussion with L. J. Rogers, M.Sc., B.E., members of the staff of National Oil Pty. Ltd. and the Department of Engineering Technology, University of Sydney; also the technical assistance of A. J. Tow, M.Sc., University of Sydney.

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TABULATA AND HELIOLITIDA FROM THE
WELLINGTON DISTRICT, N.S.W.

By O. A. JONES, M.Sc.,
University of Queensland.

(Communicated by DR. IDA A. BROWN.)

With Plate I.

Manuscript received, May 10, 1943. Read, June 2, 1943.

SUMMARY.

The paper describes some corals collected in 1942 by Miss Basnett and Miss Colditz of Sydney University. Five species of *Favosites*, one of *Heliolites* and one of *Propora* are described, the genus *Pleurodictyum* is discussed and a new species described.

The fossils are from six different localities, and while the collections are too small in some cases to give positive evidence of the age, some indication can be given.

The corals obtained from various localities are as follow :

(A) POR. 82, PAR. MICKETY MULGA.

Favosites goldfussi d'Orbigny, *F. basalticus* (Goldfuss) var. *moonbiensis* Etheridge, *Pleurodictyum bifidum* sp. nov. The first of these ranges from the Lower to Middle Devonian, the second Middle Devonian, and is especially characteristic of the Nemingha and Moore Creek Limestones. Age : Middle Devonian.

(B) POR. 206, PAR. MICKETY MULGA.

Pleurodictyum bifidum sp. nov. Age : Probably Middle Devonian.

(C) DUBBO ROAD, 12 MILES FROM WELLINGTON.

Favosites bryani Jones. This form is very characteristic of the lower Middle Devonian Murrumbidgee beds and is also found in the Lower Devonian Garra beds.

(D) POR. 241, PAR. MICKETY MULGA, WELLINGTON, N.S.W.

Propora sp. No deduction as to age.

(E) POR. 50, PAR. CURRA.

Favosites bryani. Age : Lower Middle Devonian or Lower Devonian.

(F) POR. 119, PAR. VEECH.

Favosites sp. sp. nov. ? No deduction as to age can be drawn.

(G) WILLOWTREE CREEK, ATTUNGA.

Favosites ? *goldfussi* d'Orbigny. Age : ? Devonian.

(H) ONE QUARTER MILE N.E. OF APSLEY R.S. on the road to the dredge, Wellington.

Favosites richardsi Jones, *Heliolites daintreei* Nich. and Eth. (fourth group). The former is unknown outside the Upper Silurian and in fact this is the first
C—June 2, 1943.

record outside the type area—Yass, N.S.W. The latter is known from the Upper Silurian of Yass, the Lower Devonian of Molong, N.S.W., and the Devonian of the Broken River, N. Queensland. The age may therefore be taken as Upper Silurian.

SYSTEMATIC DESCRIPTIONS.

MADREPORARIA TABULATA.

Genus *Favosites* Lamarck.

Favosites goldfussi d'Orbigny.

Favosites goldfussi (partim) d'Orbigny, 1850, p. 107 (fig. 3b of Goldfuss, 1829 only).

For synonymy, description and figures, see Jones, 1936 and 1937.

Remarks : *Favosites goldfussi* as a member of the *F. gothlandicus*-*F. goldfussi* group was discussed by Hill and Jones, 1940, pp. 191-3, where the similarity between *F. gothlandicus* forma *multiplora* and *F. goldfussi* was pointed out. The specimen from Portion 82, Parish Mickety Mulga lies between *F. gothlandica* forma *multiplora* and *F. gothlandica* forma *forbesi*, but nearer to the former, and might be called either *F. goldfussi* or *F. gothlandica* forma *multiplora*. The adult corallites are 1.75 to 2.5 mm. in diameter, slightly smaller than usual; the walls are thick and the septal spines long and numerous, though somewhat obscured by recrystallisation; the tabulæ are complete, usually horizontal, 3 or 4 in a space of 3 mm.; the mural pores are in at least three rows.

A specimen from Willowtree Creek, Attunga, may be *F. goldfussi*. It is however excessively recrystalline, so that identification is very doubtful. Septa are numerous but apparently fairly short. The mural pores may be in two rows and there are 6 or 7 complete tabulæ in a space of 3 mm.

Range : Lower and Middle Devonian (Garra beds, and Nemingha and Moore Creek limestone).

Localities : Portion 82, Parish Mickety Mulga, Wellington District, N.S.W., and ? Willowtree Creek, Attunga, Tamworth District, N.S.W. (Univ. of Sydney Nos. 6252 and 5246.)

Favosites basalticus (Goldfuss) var. *moonbiensis* Etheridge.

Favosites basaltica (Goldfuss) var. *moonbiensis* Etheridge, 1899, pp. 164-5, pl. xxiv, figs. 1, 2.

For synonymy and description, see Jones, 1937, p. 96.

Remarks : The one specimen is poorly preserved but is typical of the variety *moonbiensis* in every way except that the spacing of the tabulæ is rather more variable than in the specimens from Tamworth—2 to 4 in 1 mm. The mural pores are about 0.25 mm. in diameter in one row in the centre of the faces.

Range : Middle Devonian.

Locality : Portion 82, Parish Mickety Mulga, N.S.W. (University of Sydney, 6250.)

Favosites bryani Jones.

Plate I, figures 1, 2.

Favosites bryani Jones, 1937, pp. 96-7, pl. xv, figs. 3-6.

Favosites bryani Hill and Jones, 1940, pp. 190-1, pl. v, fig. 2.

Remarks : A specimen from portion 206, Parish Mickety Mulga and one from portion 50, Parish Curra, Wellington district, belong to this species. The

corallites are 1 to 1.25 mm. in diameter, the walls moderately thick, and the corallite angles rounded. Both are recrystalline but the septal spines appear to be of the form typical of this species—long, slender, sharply pointed, upwardly directed spines. The arrangement of the mural pores is not apparent. The tabulæ are variable in number, 7 to 11 in a space of 3 mm.

Range: Lower Devonian to lower Middle Devonian.

Localities: Dubbo Road, 12 miles from Wellington, and Por. 50, Par. Curra, both in the Wellington district, N.S.W. (University of Sydney 6254 and 6253.)

Favosites sp. sp. nov.?

Plate I, figures 3, 4.

Remarks: A specimen from portion 119, Parish Veech (University of Sydney No. 5290) is probably a new species, but being poorly preserved and a single specimen, I refrain from creating a new name for it.

The corallum is massive, the corallites regularly 1.5 mm. in diameter, the walls slightly dilated but the angles little rounded. No septa show in the transverse section but it is much recrystallised and there are indications in the longitudinal section that septa *may* be present. The mural pores are round, large—0.3 mm. in diameter—in a single row in the faces of the corallites. The tabulæ are complete, thin, regularly spaced, 7 or 8 in a space of 3 mm.

Locality: Portion 119, Parish Veech, Wellington, N.S.W. (University of Sydney 5290.)

Favosites richardsi Jones.

Plate I, figures 5, 6.

Favosites richardsi Jones, 1937, pp. 89-90, pl. xii, figs. 2, 3.

Remarks: The specimen (University of Sydney No. 7278) is completely typical of this species. The corallites are as usual of two orders of size, but this has been shown to be an environmental condition and not of specific value in *F. forbesi* (Jones, 1936) and unpublished work on *F. richardsi* confirms this. The larger corallites have 8 to 11 sides, thus becoming nearly round, and are 3.5 to 4 mm. in diameter. The smaller corallites have 4 to 6 sides and are 2 to 2.5 mm. in diameter, but there are also many young, smaller corallites, triangular or four-sided. The corallite walls are thin or very slightly dilated. The septal spines are numerous, short, with a broad base but sharply pointed. The tabulæ are complete, thin, 3 to 6 in 3 mm. The mural pores are in two rows on the faces of the smaller corallites but the arrangement has not been observed on the larger faces of this specimen.

Range: Upper Silurian.

Locality: A quarter of a mile north-east of Apsley R.S. on the road to the dredge, Wellington, N.S.W. (University of Sydney 7278.)

Genus *Pleurodictyum* Goldfuss.

Pleurodictyum Goldfuss, 1829, p. 113. Genoholotype: *P. problematicum*, *ibid.*, p. 113, pl. xxxviii, figs. 18 a-g. Lower Devonian, Eifel district and Nassau, Germany.

? *Michelinia* de Koninck, 1842, p. 29. Genolectotype (see Edwards and Haime, 1850, p. lx) *Calamopora tenuisepta* Phillips, 1836, p. 201, pl. ii, fig. 30. Lower Carboniferous, Holland and the Mendips.

Diagnosis: Cerioid Favositidæ, walls dilated, septa spinose, the spines sometimes arising from the free axial edges of very short lamellæ, sometimes

directly from the walls; tabulæ present, sometimes spinose; mural pores numerous. Topotypes usually (? always) have a worm case in the base.

Remarks: The above diagnosis is based on four topotypes of the genotype (from Oberstatfeld, near Gerolstein, Eifel) which are all internal moulds, as is the case with all topotypes known. The deduction of the complete structure of the coral from these internal moulds is difficult but there is no doubt concerning the polygonal shape of the corallites, the thick walls and the presence of numerous small mural pores, which in *P. problematicum* are usually in two, sometimes three, rows. The septal spines show as numerous round pits which sometimes are situated in a single row in a longitudinal groove, representing a short lamella; many of the spines, however, arose directly from the walls, there being no trace of any groove; and the character varies from corallite to corallite and from specimen to specimen, some corallites having several grooves, most having only one groove in the centre, other pits to either side not being in grooves, one specimen I examined having as far as I could see only one groove on one corallite, none on the remainder.

In my opinion there were almost certainly tabulæ for, firstly, on many of the moulds of the corallites there are transverse striations which can only represent ridges left when tabulæ were broken away; it may be thought remarkable that all the tabulæ were broken away before the corallites were filled and the other tissues dissolved, but the tabulæ were thin delicate structures while the walls were thick and the spines short; perhaps the tabulæ were thinner and more delicate than usual in the Favositidæ; further, the corallites were short and the corallum low and spreading, almost discoidal; secondly, in the centre of each mould are a few corallites perpendicular to the bedding planes of the rock and in several instances the surface of these is covered with numerous small shallow pits which represent more or less vertical spines. The only structures on which these spines could have been based were tabulæ.

Roemer (1883, p. 425), Hall (1876), C. L. and M. A. Fenton (1936, p. 23), Lang, Smith and Thomas (1940, pp. 84 and 102) and others consider that *Michelinia* de Koninck is a synonym of *Pleurodictyum*, although Roemer considered that tabulæ were absent in the latter. This can only be finally decided by an examination of topotypes of *M. tenuisepta* (Phillips) de Koninck, the genotype of *Michelinia*. In the meantime, basing this opinion on published descriptions and figures, I agree that most species of *Michelinia* should be placed in *Pleurodictyum*. Nicholson (1879, p. 149) describes "intramural canals" in *P. stylophorum* (Eaton) but not in *P. problematicum*. I have not observed them in the latter species, nor so far as I know has any other writer. C. L. and M. A. Fenton do not mention them in *P. stylophorum*. Nicholson considers them to be of the same nature as similar structures which he described in *Columnopora*. Cox, 1936, refers the latter to *Calapoecia* Billings, and considers the "intramural canals" to be the result of some boring organism.

Pleurodictyum is not clearly distinct from the thick walled *Favosites*. Three features may be considered in this connection—lamellar septa, spinose tabulæ and strong holotheca. If the first be taken as diagnostic a number of forms, including that to be described below, without lamellar septa but with the other two features, must be removed from *Pleurodictyum*; but the presence of spines on the tabulæ, a character which varies much from species to species, and the presence of a stronger holotheca than is usual in *Favosites* are not enough on their own to justify separation of the two genera. The whole group of forms stands in need of revision.

Pleurodictyum bifidum sp. nov.

Plate I, figures 7, 8.

Holotype: The specimen 6251 in the collection of the University of Sydney from Por. 82, Par. Mickety Mulga, Wellington, N.S.W. Age: Middle Devonian.

Diagnosis: *Pleurodictyum* with numerous spinose septa, some of which are bifid, numerous irregular complete and incomplete tabulæ, mural pores large and rare.

Description: The corallites are polygonal but the angles are rounded by the dilatation of the walls which makes them as much as 1.25 mm. in thickness. The diameter of the corallites is 4 to 6 mm. The septa are spinose and very numerous, arranged in longitudinal rows which number seven or more on each corallite face. The spines are stout but usually sharply pointed and about 5 per cent. divide near their axial ends into two (? sometimes three) branches, an unusual and important character, upon which I have based the trivial name. This appears to be a type of rhabdacanthine septa (Hill, 1936) but on a larger scale than any yet described, and unfortunately the coral is not sufficiently well preserved to observe the trabeculæ and confirm this suggestion. The tabulæ are thin, numerous, 10-13 in 5 mm., complete and incomplete in about equal numbers, horizontal or oblique, sometimes deeply invaginated. The mural pores are large, 0.25 mm. in diameter; their arrangement has not been definitely observed, but there is some evidence to suggest two rows, each row fairly close to the corallite angle.

Remarks: I know of no species with which this is closely comparable, the very large number of septa and their frequent bifid nature are very striking characters.

Localities: Por. 82 and Por. 206, Par. Mickety Mulga, Wellington, N.S.W. (6251 and 5287 University of Sydney collection). Middle Devonian.

MADREPORARIA HELIOLITIDA Jones and Hill.

Family Heliolitidæ.

Genus Heliolites Dana.

Heliolites daintreei Nicholson and Etheridge.

Plate I, figures 9, 10.

Heliolites daintreei Nicholson and Etheridge, 1879, p. 224, pl. xiv, figs. 3, 3a.

Heliolites daintreei Jones and Hill, 1940, pp. 199-203, pl. vi, figs. 1-5; pl. vii, figs. 1-5; pl. viii, figs. 1-8; pl. ix, fig. 1.

For synonymy, diagnosis, etc., see Jones and Hill, 1940.

Remarks: This is a variable, long-ranged species, divided by Jones and Hill into four, ill-defined groups. The specimen under consideration falls into group four. The tabularia are 1.75 to 2.5 mm. in diameter, rather larger than usual, with none to six rows of tubuli, and 0 to 4 mm. between the tabularia. The tabularia are in contact in only one place in the section and usually there are 2-3 rows of tubuli between. The walls of the tabularia, the tabulæ and sola are typical of the group. The septa are largely obscured by recrystallisation but show in places in the transverse section, arising from the wall between the slight angles formed where two tubuli meet the wall. The walls are sometimes crenulate, and then the septa arise from the crenulations. That the septa are long spines upturned axially is shown in transverse section by their abrupt truncation and the occasional occurrence of apparently detached fragments towards the centre of the tabularia.

Range: Group four ranges in Australia from Upper Silurian to Middle Devonian.

Locality: One quarter of a mile N.E. of Apsley on the road to dredge, Wellington, N.S.W. (University of Sydney 7272.)

Genus *Propora* Edwards and Haime.

Propora sp.

Plate I, figure 11.

Remarks: A single specimen is an undescribed species of *Propora*. The state of preservation is poor, but the transverse section shows the tabularia to be thick walled and crenulate with long septa, stout at the base but rapidly becoming thin, arising from the crenulations. The septa reach or nearly reach the centres of the tabularia and are prolonged in the other direction outside the tabularia into the reticulum. The longitudinal section is obscure so that the character of the septa cannot be determined. The reticulum consists of testæ, but beyond this the characters cannot be seen. Of described species it may be close to *Propora tubulata* Lonsdale but further comparison must await better specimens. It is quite unlike *P. conferta* Ed. & H., the only other species recorded from Australia (see Jones and Hill, 1940, p. 209).

Locality: Por. 241, Par. Mickety Mulga, Wellington, N.S.W. (University of Sydney 7279.)

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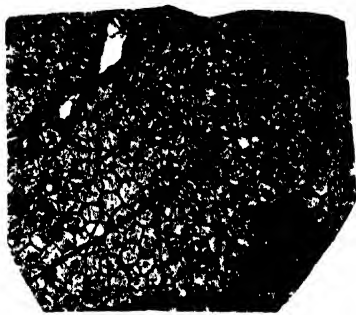
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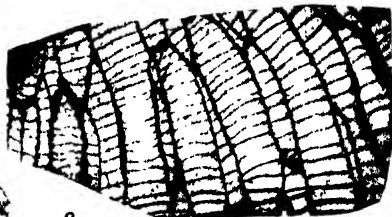
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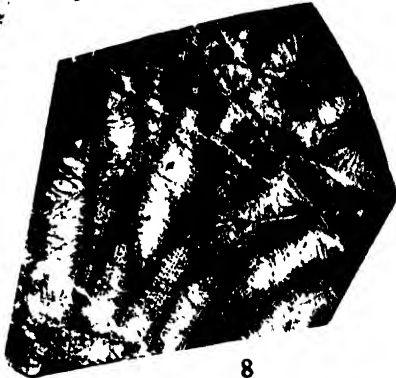
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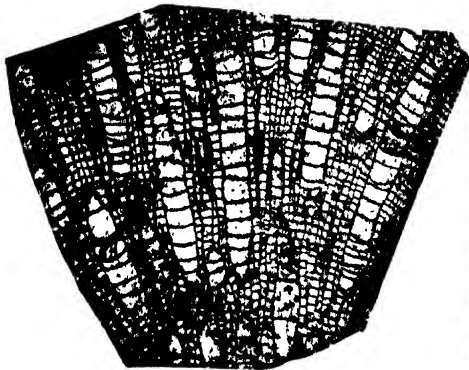
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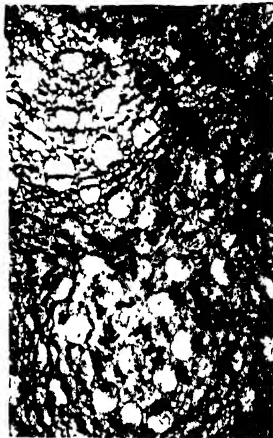
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11

EXPLANATION OF PLATE.

All figures $\times 2$ approximately.

- Figs. 1, 2.—*Favosites bryani* Jones. 1, transverse ; 2, longitudinal section. Dubbo Road, 12 miles from Wellington. (S.U. 6254.)
- Figs. 3, 4.—*Favosites* sp. nov. ? 3, transverse ; 4, longitudinal section. Por. 119, Par. Veech, Wellington. (S.U. 5290.)
- Figs. 5, 6.—*Favosites richardsi* Jones. 5, transverse ; 6, longitudinal section. One-quarter mile N.E. Apsley R.S. on road to dredge, Wellington. (S.U. 7278.)
- Figs. 7, 8.—*Pleurodictyum bifidum* sp. nov. Holotype. 7, transverse ; 8, longitudinal section. Por. 82, Par. Mickety Mulga, Wellington. (S.U. 6251.)
- Figs. 9, 10.—*Heliolites daintreii* Nich. & Eth. 9, transverse ; 10, longitudinal section. One-quarter mile N.E. Apsley R.S. on road to dredge, Wellington. (S.U. 7272.)
- Fig. 11.—*Propora* sp., transverse section. Por. 241, Par. Mickety Mulga, Wellington. (S.U. 7279.)
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THE ETCH FIGURES OF BASAL SECTIONS OF QUARTZ. THEIR USE IN THE ORIENTATION OF WATERWORN CRYSTALS.

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With Plates II-III and nine text-figures.

(Presented by permission of the Under-Secretary for Mines.)

Manuscript received, May 11, 1943. Read, June 2, 1943.

INTRODUCTION.

This paper sets out the results obtained by etching sections of quartz cut perpendicular to the optic axis. It also examines the possibility of orientating sections, cut in this plane, in which the positions of the prism faces are unknown.

The main use of quartz is for the manufacture of quartz plate resonators. For this purpose the plates have to be cut in a definite relationship to the crystal axis, in order to obtain the optimum temperature-frequency coefficient and eliminate secondary resonances. The margin of error permitted in this operation is very small and in order that the cutting can be carried out with the required degree of accuracy, the positions occupied by the prism faces must be known fairly accurately.

A certain quantity of waterworn quartz crystals of high quality is available, which cannot be used for piezo-electric purposes unless the positions of the prism faces are known reasonably accurately. The position of the optic axis can be obtained with an accuracy of ± 10 minutes by means of a polariscope (Booth and Sayers, 1939). The position of a plane perpendicular to all prism faces thus being known, it still remains, before the orientation is completely determined, to fix the positions these faces occupy in this plane. The order of accuracy required for this operation is not so great as that for the determination of the position of the optic axis.

The work, the results of which are set out in this paper, was originally undertaken in order to see whether a way of solving this problem could be found, without recourse to X-ray methods.

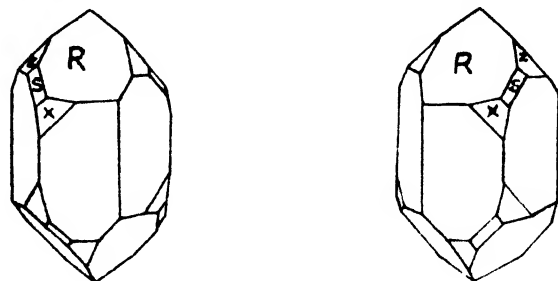
A summary of some of the properties of quartz has been included in order to make the results detailed easier to follow.

Properties of Quartz.

Quartz crystallises in the hexagonal system and occurs as two varieties, α -quartz and β -quartz (Bragg and Gibbs, 1925; Gibbs, 1926). α -quartz, which forms at temperatures below 575°C. , has only trigonal symmetry and possesses the property of piezo-electricity. Quartz is enantiomorphous, the form assumed depending on whether the spiral atomic structure is right- or left-handed. This variation in internal structure is reflected in a variation of the outward form by the disposition of the subsidiary x and s faces, as shown in Figure 1.

The *Bulletin of the Imperial Institute* (1938) has given the following notation for piezo-electric quartz decided upon by the Department of Scientific and Industrial Research: The principal crystallographic axis, which is an axis of threefold

symmetry and coincides with the optic axis, is referred to as the Z axis. At right angles to this axis there are the three crystallographic axes, which pass through the intersections of the prism faces. These axes of diagonal symmetry are known as the X axes. A further set of three Y axes, in the same plane but



Left-handed

Right-handed

Quartz Crystals

FIGURE 1

perpendicular to the X axes, is assumed for piezo-electric purposes. Under compression or tension along the X axes, the opposite ends take up opposite charges, the signs of these charges depending on whether the crystal is right- or left-handed. The positions of the X and Y axes are shown in Figure 2. The Z axis would be perpendicular to the plane of the paper through O .

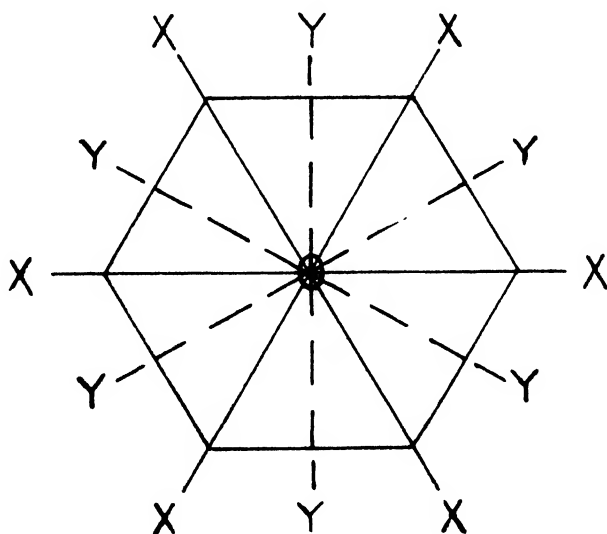


FIGURE 2

Quartz crystals are almost invariably twinned. The only types of twinned crystals considered in this paper are those which consist of complete interpenetration twins. Twinning of this form can take place in three different ways. In all cases the Z axes of the two parts of the twin crystal are coincident. In

type (a) a right- or left-handed crystal may be concerned. It is known as electrical twinning to distinguish it from types (b) and (c), which are known as optical twinning, because they can be recognised by optical means. In types (b) and (c) both a right- and left-handed crystal are concerned.

(a) One portion of the crystal may be considered as being rotated through 180° around the Z axis, with respect to the other portion. This can be detected by the appearance of x or s faces upon adjacent corners. The R of one individual coincides with the z of the other, so that the pyramid faces may consist of some parts which are bright and others dull.

(b) This occurs when a right-handed crystal is united with a left-handed crystal, so that the R faces of the two individuals coincide. It can be recognised by the appearance of both right- and left-handed x or s faces at the base of the same pyramid face. From the frequency of occurrence of this type of twin crystal in specimens from Brazil, it is often spoken of as a Brazil twin.

(c) This occurs when a right- and left-handed crystal are so united that one individual is rotated through 180° around the Z axis with respect to the position taken up in (b) above, thus bringing the R face of one individual into coincidence with z face of the other. This type can be recognised by the appearance of the two types of x or s faces on the same corner.

In the same crystal a combination of two forms can and very often does take place. It is only a very small proportion of the crystals found, in which optical and/or electrical twinning do not occur. Either type ruins the crystal for piezo-electric purposes as the X axes of the two portions are developed in opposite senses. Where a crystal consists of one major individual with only small portions which are twinned, the untwinned portion can be used and the remainder rejected.

Etching of Basal Sections.

The sections cut perpendicular to the optic axis were etched with hydrofluoric acid. Total periods of etching varied from 10 minutes to 16 hours, with a reading taken on one crystal after 72 hours. Single specimens were examined after etching for periods of 10 minutes at a time, over several hours. Prior to etching the surfaces were prepared by being ground flat with carborundum powder. Three grades of powder were used, 4F, 3F and 220. Care had to be taken to remove all saw-cut marks, as these gave parallel bands, which influenced the reflections to some extent. The effects of the different surfaces on the results obtained are discussed below.

The sections were placed on the rotating stage of a microscope, obliquely illuminated by a source of light and the reflected light examined through the microscope. The same effect could have been obtained by keeping the sections in a fixed position and rotating the beam of light.

The light source used gave a reasonably concentrated beam, although it was not absolutely parallel. This source was set up about three feet from the microscope and directed through a slit in a piece of cardboard placed close to the microscope, the slit being just sufficiently large for the field of view to have full overall illumination. The light was so directed that when the beam was parallel to a prism face of the section, the scale reading of the stage of the microscope was zero. The angle of incidence for most of the readings was about 70° measured from the perpendicular. The effect of varying this angle is discussed below.

The etch markings (see Plate II) commence as triangular pits and with deeper etching become triangular hillocks. Booth and Sayers (1939) have postulated that the etch faces are curved. This is confirmed by the results given in this paper. The incident light is reflected from the faces which form the sides of these pits or hillocks, so that during a complete rotation of the stage there are

three positions of maximum illumination, between which there is relative darkness. These three positions are not at exactly 120° with one another, nor do they bear a constant relationship to the X (or Y) axes as may have been expected.

In the results that follow each position of maximum illumination has been measured as an angle, positive or negative, from the nearest 120° position, and the average of the three readings thus obtained taken as the angle in the horizontal plane at which maximum reflection is obtained for that particular section for the time of etching and strength of acid used. For instance, if maximum reflections were obtained at 8° , 131° and 251° , these positions would read as 8° , 11° and 11° respectively, the average figure or reading taken being 10° . Using this method of recording results, a zero (or $\pm 60^\circ$) reading would mean that maximum reflection occurred when the beam of light was parallel to a prism face, a $\pm 30^\circ$ (or $\pm 90^\circ$) reading would correspond to the beam of light being perpendicular to a prism face, and so on. The sign of the reading so obtained would depend on the direction of rotation of the stage, being positive for anti-clockwise rotation and negative for clockwise rotation with the microscope used. It should be noted that a reading of -10 is equivalent to $+110$, -20 to $+100$, etc. If the light is parallel to one prism face and the section is turned around in a clockwise direction until the adjacent prism face is parallel to the light, still keeping the scale reading zero, a rotation of the stage until the scale reading is 60° will bring the section into its original position. It can be seen therefore, that a reading of $60+\theta$ would be equivalent to a reading θ depending on which prism face was originally parallel to the light, when the scale reading was zero.

The angle at which maximum illumination occurs varies in a very complicated manner, depending on the length of time of etching and strength of acid used. Sections were taken and etched for periods as short as ten minutes at a time and the angles obtained plotted on a curve, with period of etching as the abscissa and angle at which maximum illumination occurred as the ordinate. Although the way in which the angle changes is complicated, the change seems to follow a definite order and is not haphazard. It is regretted that with the time available it was not possible to read several crystals through a complete cycle. A composite curve has been constructed by compounding the results from the etching of several sections which have been read at short intervals over different parts of this curve. The longest total period of etching during which readings were taken continuously was 16 hours. In Figure 3, several curves obtained are shown, together with the composite curve constructed from them. Corresponding parts of the curves are similarly marked by the letters A , B , C , etc. The continuous parts of the curves are where the readings have been taken every ten or fifteen minutes and the broken curves are portions interpolated from analogy with other curves. Small circles on these broken sections show actual readings taken. The construction of a composite curve as being representative of any crystal has been rendered difficult by the fact that the individual curves are not directly comparable, and this even applies to different parts of the same curve, owing to the strength of the acid used varying. Large variations in the strength of the acid used were brought about mainly by lack of knowledge, in the early stages of the work, as to the period for which the acid would maintain a reasonably high rate of attack and secondly by one bottle of acid, although newly opened for the work, having apparently lost most of its strength during storage. The fact that the angle was not changing could not be used as an indication that fresh acid was required, because there are apparently parts of the curve for which the rate of change is only small, irrespective of the strength of the acid used. Although differences in strength of acid may change the apparent shape of the curve, it is considered that it would not affect the values of the maxima, minima and points of inflection. It should be pointed out at this

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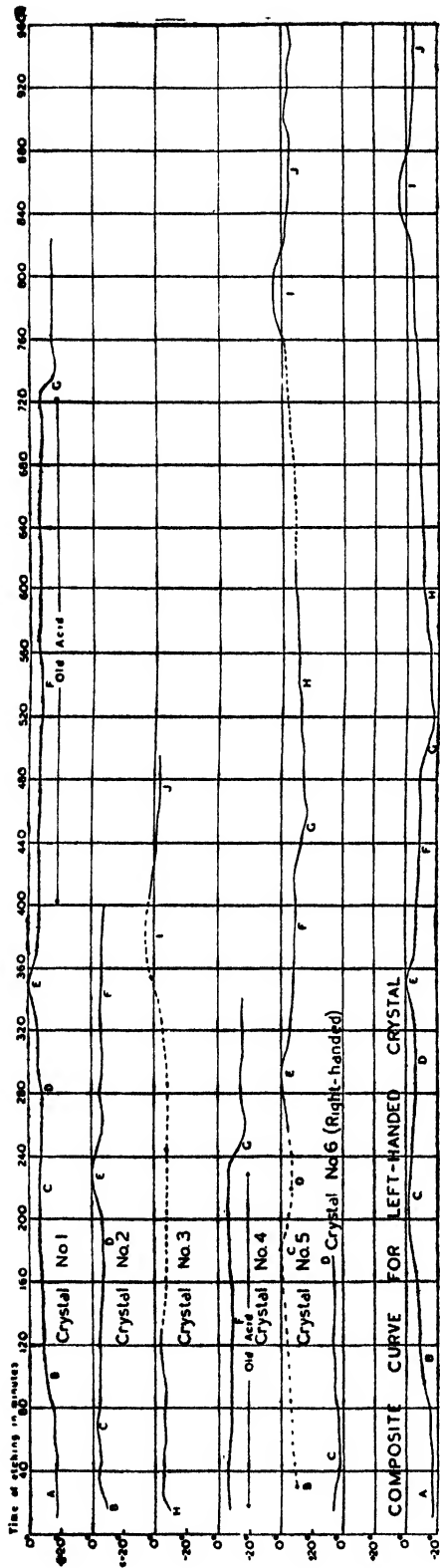


FIGURE 3

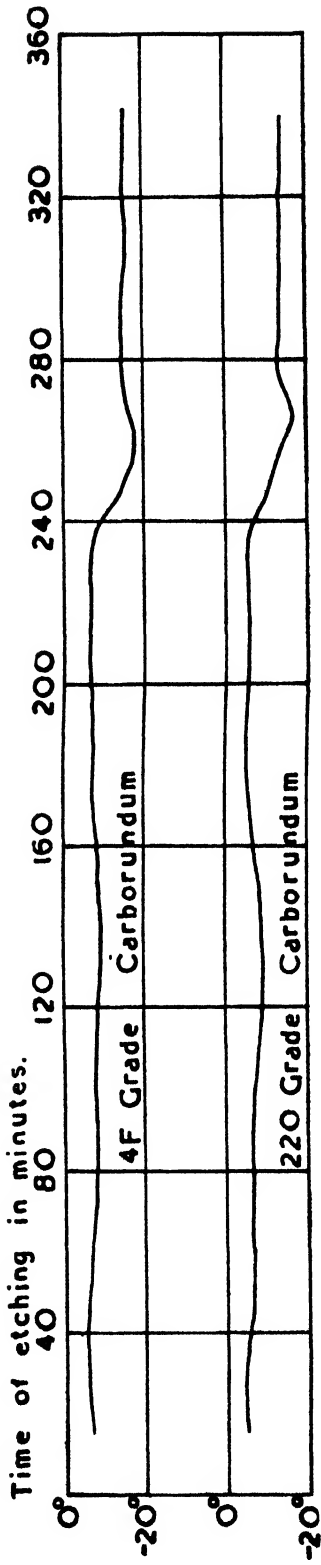


FIGURE 4

stage that the composite curve shown is only intended to represent the most likely curve on which the positions of maximum illumination would fall. The variation is too complicated to be completely delineated from the amount of work done. It is hoped that, at a later date, further work may enable the details of the curve to be shown more exactly. It will be noted that the curves for different crystals do not commence at the same figure, but may begin at practically any point on the composite curve. Since the point of commencement is not fixed, the same point on the curve would correspond to different depths of etching for different crystals. This would probably have an effect on the rate of change of the angle of maximum reflection and also to a few degrees on the actual values of minor positions of maxima or minima and points of inflection. It is not considered that it would affect the values of the absolute maximum or minimum for the whole curve.

The curves obtained for right- and left-handed crystals are similar in shape, but opposite in sign at corresponding parts of the curve. Right-handed crystals commenced with a positive reading and left-handed with a negative one in all cases examined. This difference will be further discussed under twinning.

The composite curve for a left-handed crystal will now be considered in some detail. At *A* the curve is at its minimum value of -17° , a value which is repeated at *G*. From *A* the value changes relatively quickly to about -10° at *B*. Further on at *C* there is a maximum value of about -3° . This corresponds to the values obtained with crystals Nos. 2 and 5. The value for crystal No. 4 was 0° , but as this point was only fixed by a single reading it may be in error. This maximum at *C* is -7° for crystal No. 1. This may be due to this crystal being much more deeply etched than either Nos. 2 or 5 by the time this point was reached. The value of the minimum at *D* varies from -7° to -9° for different crystals. The maximum value of 0° at *E* seems to be one of the most definite points on the curve, because it was obtained with all three crystals measured, which were considered to correspond to the early portion of the composite curve. After the maximum at *E*, there is a relatively flat portion of the curve which varies gradually from -6° to -10° . This portion was unduly prolonged in the curves for crystals Nos. 1 and 4, owing to the bottle of old acid, referred to previously, being used. From -10° , the curve changes suddenly to -17° at *G*, which is the absolute minimum value reached at any point of the curve. The suddenness of this change in crystals Nos. 1 and 4 may be partly due to the use of fresh acid, which was definitely stronger than the average acid used in the rest of the work. For this reason, the shape of this portion of the composite curve was taken from that for crystal No. 5, which was considered more representative of what would be obtained with medium strength acid. From *G* there is a normal rate of change to about -12° to -10° at *H*. Between *H* and *I* there are relatively few readings, on which to base the curve. The value of the maximum at *I* is about $+4^\circ$. The values quickly change again to negative and are about -6° at *J*, which is the furthest point reached in any curve. The form taken by the composite curve in stages later than those shown is unknown. One section which gave a reading of -10° after approximately one hour's etching read $+10^\circ$ after a further 16 hours. From this it seems possible that a section which gave a reading of -17° at one stage may vary and give a reading of $+17^\circ$ at a later stage, in which case the composite curve would repeat itself on the opposite side of the zero position.

The small difference obtained by varying the surface finish is well shown in Figure 4. This test was made on two portions of the same section of crystal.

The section was first surfaced using 4F grade carborundum and then broken across the middle. One piece was then completely resurfaced using 220 grade carborundum. The similarity between the two curves obtained is striking. In actually taking the readings, the position of maximum illumination seemed

somewhat easier to judge in the section having the coarser finish, but the curve obtained from the other section is somewhat smoother. The more uneven curve in the former case may be due to reflections from the rougher surface interfering to some extent. It is doubtful if there is anything to be gained by using a finer finish than that obtained with 220 grade carborundum.

Variation in the angle of incidence of the light has no effect over quite a large range. This is shown in the graph, Figure 5. Below an angle of 52° the

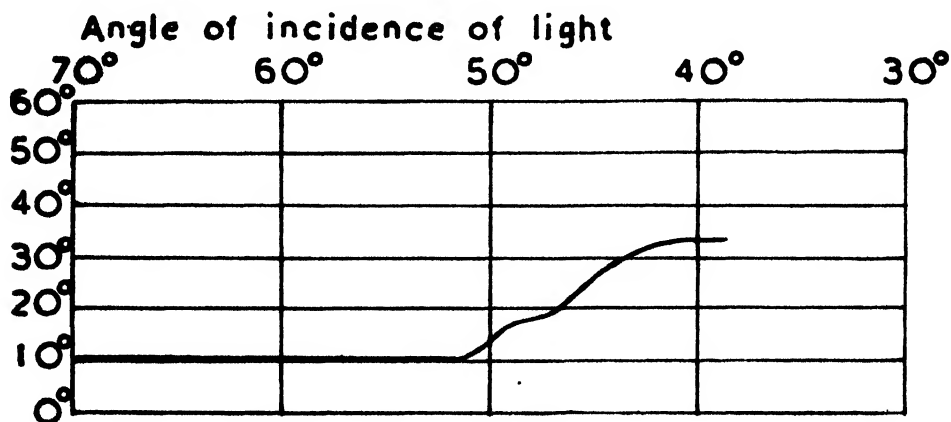


FIGURE 5

change is however very marked. This variation in the angle of maximum illumination as the angle of incidence changes would seem to be due to the curvature of the etch faces. The effect of varying the angle of incidence was only measured on one section. If the etching had been lighter or deeper, the critical angle of incidence, at which the angle of maximum illumination started to change, might have been different. Still the curve does seem to show that irrespective of the depth of etching, there would be a considerable range over which the angle of incidence could be varied without changing the readings obtained.

In etching the sections of quartz, the acid tends to attack along lines of weakness in the crystal structure, and as a result the faces of the etch figures also bear a relationship to this structure. The fact that the relative positions of these etch faces is not constant may be due to the distorted spiral nature of the atomic structure of α -quartz. If a few layers only of the atomic structure be considered, the planes in which the packing of the atoms is closest may not be the same as when the neighbouring layers are considered too. If it were so it would mean that the relationship of the etch faces to the crystal faces would change with depth of etching.

An interesting point is the relationship of the readings obtained on opposite sides of a slab. This relationship is best explained by reference to Figure 6.

In the following it is assumed that the etching of both sides of the slab has reached the same stage of development and that the light is incident from the right. If the angle at which maximum reflection is obtained is taken as 10° , the readings obtained for the three positions of maximum illumination, with the slab in the position shown in Figure 6 (a), are approximately 10° , 130° and 250° , and an etch pit would be orientated as shown by the triangle *abc*. The same reading would have been obtained had *CD* or *EF* been in the position occupied by *AB*. When the slab is reversed as shown in Figure 6 (b), the readings obtained are 70° , 190° and 310° , and an etch pit would be as shown by the triangle *def*.

It will be noticed, however, that the light is now falling from the direction of corner *F* instead of corner *C*. If allowance were made for this fact by deducting 180° from the above readings, they would become 10° , 130° and 250° , as on the other side of the slab.

If the position of the pit *abc* be projected through the slab on to the other surface, it will occupy the position $a_1b_1c_1$. From studying the relationship between the triangles $a_1b_1c_1$ and *def*, it will be seen that the bisectors of the angles between the positions for maximum illumination on one side of the slab and the projections of the positions of maximum illumination on the other side of the slab, that is, between the perpendiculars to the sides of the triangles, are parallel to the prism faces. With one slab examined in this way, it was found that after one hour's etching the opposite sides of the slab gave the same reading. The slab was then etched for a further 16 hours and the two sides of the slab again gave equal readings, which, however, differed from those obtained after

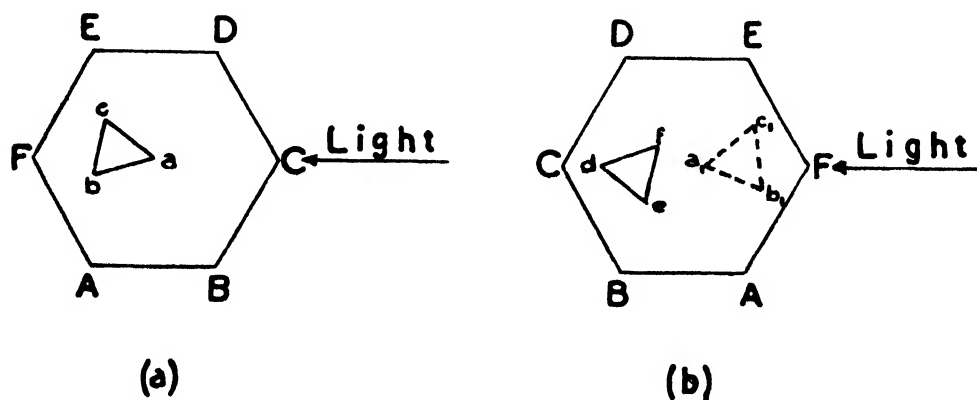


FIGURE 6.

one hour. This may have been a coincidence, but if the readings on opposite sides of a slab were always equal, it would mean that the difference in the starting points for the curves for different sections were due, not to the relationship of the ground surface to the crystal structure, but to the conditions of etching, such as temperature and strength of acid and relative temperature of the slab itself, when placed in the acid.

When a crystal is twinned, each portion of the section develops its own curve. No matter what type of twinning is present, each twinned portion of the section reaches the same degree of development after the same period of etching.

If a crystal is electrically twinned (type (a)), one portion is rotated through 180° with reference to the other. In this case maximum illumination is obtained at approximately every 60° , the alternate readings being from the different twinned individuals. (See Plate II.) An interesting point is that the differences of each of these six readings from the average, taken in order, lie on a fairly regular curve. This fact was used as a check on the accuracy of the readings. Any reading to which this did not apply was always found to be inaccurate when checked. Portions of the curves obtained with one crystal are shown in Figure 7. Part (a) shows the curves for the six positions of maximum illumination and part (b) the two curves for the mean position.

When a crystal is optically twinned, the positions of maximum illumination of each portion vary by the same amount but in opposite directions from an intermediate position. This intermediate position depends on the type of

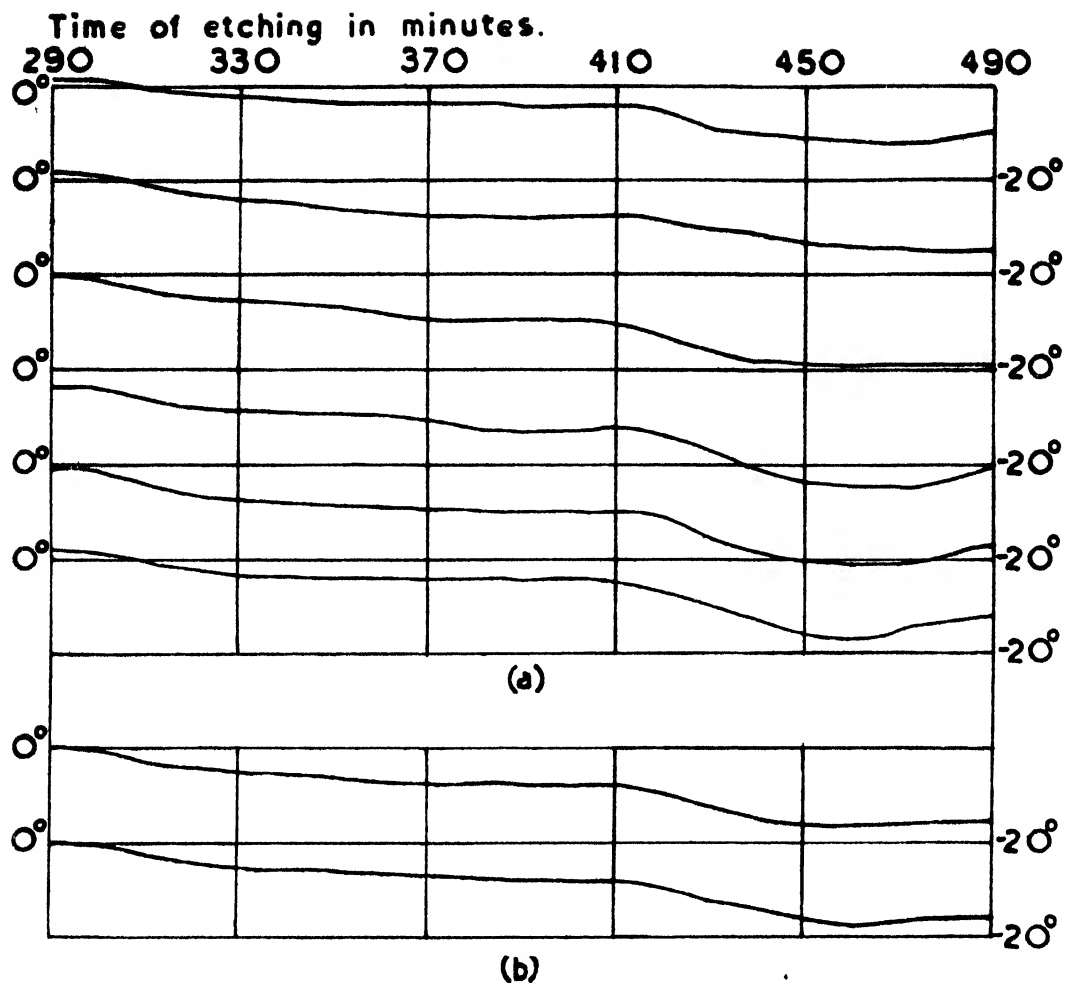


FIGURE 7

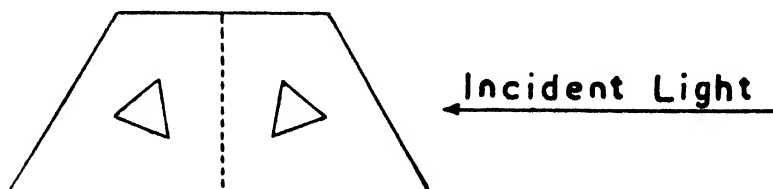


FIGURE 8

optical twinning present, but the actual value is independent of the period of etching.

When the twinning is of type (b), the intermediate position is 30° . This is made clear in Figure 8.

The right-hand side shows the shape of a triangular pit in a right-handed crystal, assuming the angle of maximum illumination is 10° . Similarly, the

left-hand side represents a left-handed crystal, being a mirror-image of the right-hand side. Maximum illumination occurs when the sides of the triangle are perpendicular to the incident light and the light is shining across the triangle. It will be seen that maximum illumination occurs for the right-hand side at 10° , 130° and 250° and for the left-hand side at 50° , 170° and 290° . The intermediate positions are, therefore, 30° , 150° , 270° . The difference between two corresponding readings for maximum illumination of the two parts of the twin varies from 26° to 60° , depending on the period of etching. Practically all optical twinning is of this type. It usually occurs as a network crossing at 60° . (See Plate III.) This network is sometimes very fine (Plate III), and if this be the case it is masked by very deep etching. At the intermediate positions, the illumination from each twinned portion is equal. Figure 9 shows the three curves obtained from an optically twinned section, the two of maximum and the one of equal illumination.

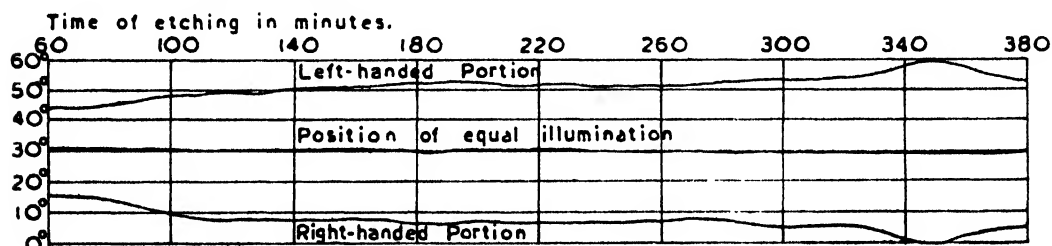


FIGURE 9

When type (c) is present, the intermediate positions are 0° , 120° , 240° . The difference between two corresponding readings for maximum illumination of the two parts of the twin varies from 0° to 34° , depending on the period of etching.

Provided etching is carried out over a sufficiently long period, types (b) and (c) can always be differentiated, as a difference in corresponding readings greater than 34° can only occur with type (b), and less than 26° with type (c).

These results are summarised in Table 1. The reading for maximum illumination, in each case, is taken as 10° , and for the sake of clearness, the

TABLE I.

Untwinned Crystal.				Type of Twinning.					
Right-handed.		Left-handed.		(a)		(b)		(c)	
A	\bar{A}	B	\bar{B}	$\bar{A}\bar{A}$	$\bar{B}\bar{B}$	AB	$\bar{A}\bar{B}$	$\bar{A}\bar{B}$	$\bar{A}\bar{B}$
10				10		10		10	
	70	50		70	50	50			50
			110		110		70		70
130				130		130	110	110	
	190	170		190	170	170		130	170
			230		230		190		190
250				250		250	230	230	
	310	290		310	290	290		250	290
			350		350		310		310
							350	350	

three positions of maximum illumination are taken as being at exactly 120° with one another. The first four columns show the readings in degrees for a right-handed and left-handed crystal and the same rotated through 180° . The other six columns show the sets of readings in degrees which would be obtained by combining any two of these.

The order of accuracy of the readings is of importance. The brightness of the reflections shows large variations as the period of etching increases. At the commencement of etching the etch markings are only shallow and the faces formed small, resulting in relatively poor reflections. However, the brightness of the reflections does not continue to increase regularly as the period of etching increases, but passes through phases where the reflections are poor. The brightest reflections would be expected when the perpendicular to the etch face bisected the angle between the incident and the reflected ray viewed through the microscope.

With average strength of reflections, readings obtained for each particular maximum reflection vary about $\pm 2^\circ$ from the mean position. This would give the average reading of the three positions of maximum illumination an order of accuracy of $\pm 2^\circ$, but as errors in the individual readings mostly compensate to some extent, the mean readings would usually vary by much less than $\pm 2^\circ$.

When optical twinning is present, between the two corresponding readings for maximum illumination there is the position at which the illumination from the two portions of the twin is equal. This position can be judged much more accurately than the positions of maximum illumination, the order of accuracy in this case being better than $\pm 1^\circ$.

Orientation of Unknown Sections of Quartz.

Two cases arise, one being when the crystal is either untwinned or electrically twinned and the other when optical twinning is present.

In the former case there may be two possible ways of orientating the section. One of these depends on etching the crystal over a sufficiently long period to obtain a curve which can be identified as some definite portion of the composite curve, so that either a maximum or minimum or point of inflection can be recognised. Whether a crystal were right- or left-handed would be known beforehand from examination in a polariscope. Unless further work were done in order to determine the composite curve more accurately, the order of accuracy to be expected from this method would not be closer than to within a few degrees. The main drawback is, however, the long period of etching which would be required, and this renders the method of very doubtful importance from an economic standpoint. The second method requires that readings be taken on both sides of an etched slab. The validity of this method depends on whether it can be assumed that the two etched faces would simultaneously reach the same stage of development. If it be so, any section can be orientated after one period of etching of any duration with an order of accuracy within $\pm 2^\circ$.

When optical twinning is present, and practically all quartz crystals have some portion which is optically twinned, the positions of equal illumination can be read with an order of accuracy of $\pm 1^\circ$. This can be done after one period of etching and the duration of this period is immaterial. For the best results the section should be etched long enough to obtain good reflections from the etched surface. The positions of equal illumination can be checked by taking the mean of the two readings for maximum illumination. If the readings for maximum illumination are either wide, that is approaching 60° , or close, approaching 0° apart, it is advisable to re-etch for a further period, because it is much harder to judge the position of equal illumination under these circumstances.

This method was tested on an unknown section. A slab of quartz cut perpendicular to the optic axis, containing the prism faces, was taken and a

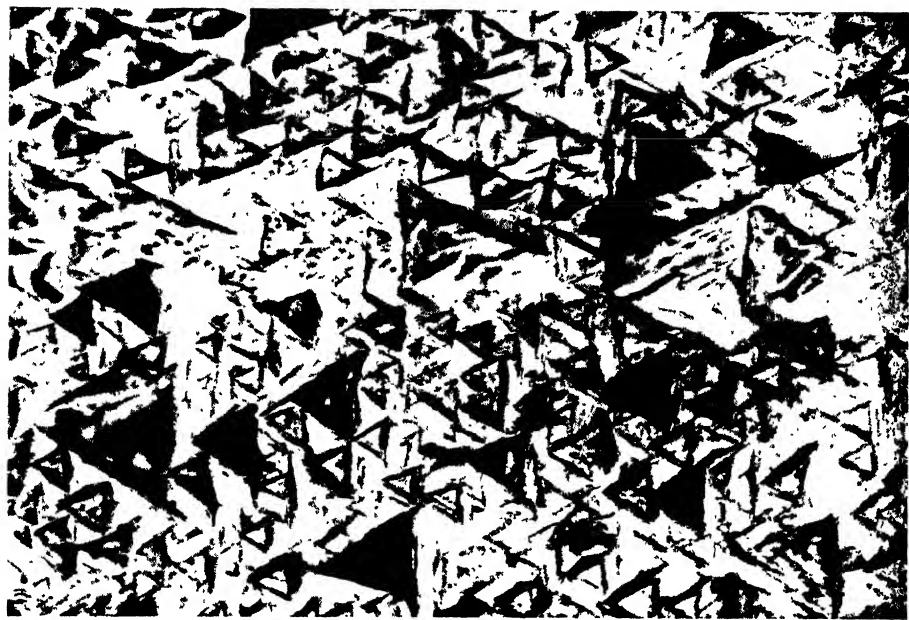


Figure 1.



Figure 2.

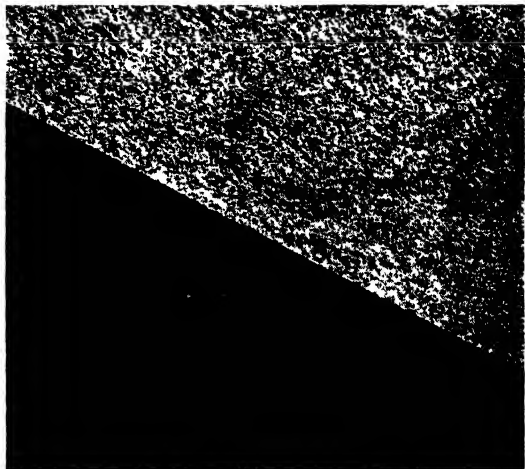


Figure 3.



Figure 4.

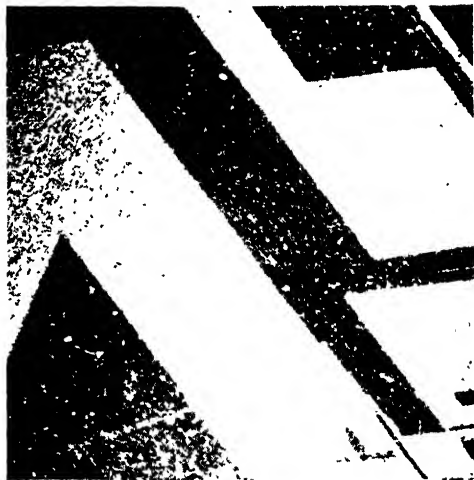


Figure 5.

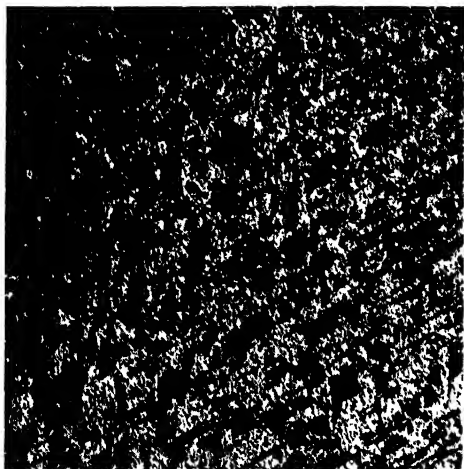


Figure 6.



Figure 7.

random cut made across the slab. The blank so obtained was kept for checking purposes and the other piece had all the remaining prism faces removed. Using this portion the relationship of the random cut to a prism face was determined and the result obtained checked from the blank. The error was only $\frac{1}{4}^{\circ}$.

SUMMARY.

Basal sections of quartz, etched with hydrofluoric acid, were rotated on the stage of a microscope and obliquely illuminated. The position of the sections that gave the maximum reflected illumination through the microscope was determined. This position varied with the duration of etching and a curve showing this variation was constructed.

While unknown sections of untwinned or electrically twinned crystals could be orientated by obtaining their curves, the process is long and tedious and the order of accuracy to be expected is not closer than to within a few degrees. If the etching on opposite sides of such a slab could be assumed to have simultaneously reached the same stage of development, it could be orientated after one period of etching to within $\pm 2^{\circ}$. When optical twinning is present, and this is the case with some portion of most crystals, an unknown section can be orientated to within $\pm 1^{\circ}$.

ACKNOWLEDGMENTS.

I wish to thank the Government Geologist, Mr. L. J. Jones, A.S.T.C., for permitting me to carry out this work; Mr. F. W. Booker, M.Sc., at whose suggestion the work was originally undertaken; and Mr. H. F. Whitworth, M.Sc., for taking the photographs accompanying this paper. I wish to sincerely thank Amalgamated Wireless (Aust.) Ltd. for the supply of all quartz sections and Miss V. Gazeley for typing the manuscript.

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For a more complete bibliography, readers are referred to the last reference.

DESCRIPTION OF PLATES.

PLATE II.

Figure 1.—Etch markings by transmitted light after 72 hours' etching. This photo shows a section which is electrically twinned. It will be noted that the triangular markings are pointing to the right in the upper portion of the photograph and to the left in the lower portion. $\times 200$.

Figure 2.—Electrically twinned section, showing one individual at position of maximum illumination.

Figure 3.—Same rotated through 60° .

PLATE III

Figure 4.—Optically twinned section, showing left-handed individual at position of maximum illumination.

Figure 5.—Same with light rotated through about 40° , bringing the right-handed individual into the position of maximum illumination.

Figure 6.—Optically twinned section, showing fine mesh structure. Left-handed individual at position of maximum illumination.

Figure 7.—Same with light rotated through about 40° , bringing the right-handed individual into the position of maximum illumination.

Figures 2 to 7 are all $\times 10$ and were all taken from different parts of the same section of one crystal.

AUSTRALIA'S MINERAL INDUSTRY IN THE PRESENT WAR.*

By H. G. RAGGATT, D.Sc.

I deeply appreciate the honour which the Society has done me by inviting me to deliver the Clarke Memorial Lecture for 1943, and it is with great pleasure that I welcome the opportunity which this occasion presents, to pay my tribute to the memory of the father of Australian geology, the Rev. W. B. Clarke.

There are no rules laid down by the Society which Clarke Memorial Lecturers are expected to follow, and you will find that a great variety of topics has been selected in the past. It is clear, however, that past lecturers have set out to treat their subjects in a way which would make them of general interest and they have all tried to keep their discourses to a length of about 8,000 words.

This lecture is a memorial to a great and versatile man whose observations covered a wide field, both in stratigraphy and economic geology. It would befit the occasion, therefore, to select a topic from one or other of those fields. Bearing in mind that stratigraphy is a difficult subject to make interesting to a non-specialist audience, and that we are engaged in the most terrible armed conflict in history, I thought it would be fitting to devote this lecture to some aspects of the Mineral Industry of Australia, and the effect of the war upon it. This audience will appreciate that there are many details which cannot be mentioned in discussing such a topic in wartime, and that this address must therefore keep mainly to generalities.

Ready access to an adequate supply of most metals and many minerals is one of the most important essentials in the prosecution of war, but it would be wearisome merely to draw up a list of metals and minerals which are of special interest at the present time and to discuss them, one by one. I propose instead to deal with the whole field in very general terms but to place the accent upon the little known, new, and unusual rather than to divide my time according to the relative importance of the various metals and minerals.

There are many ways in which the mineral industry of a country may be discussed. For the purposes of this address I propose to follow approximately the headings given hereunder:

Precious metals.

Fuels.

Iron and Steel.

Ferro-alloys; Bismuth.

Base metals other than Iron; Cadmium and Cobalt.

Light metals.

Antimony and Arsenic.

Tantalum and Columbium.

Beach Sand Minerals.

Sulphur, Sulphides and Sulphuric Acid; Phosphate Rock.

Non-metallic Minerals.

PRECIOUS METALS.

We need only consider gold, silver, platinum and osmiridium. I put the precious metals first, because *gold*, normally the most important of the group,

* The Clarke Memorial Lecture delivered to the Royal Society of New South Wales, June 23, 1943.

is the least important in this war, and thus may be dismissed in a few words. If one were seeking to compare our pre-war mineral industry with that of the present day, probably the most striking feature would be the relative unimportance of gold mining at the present time. In fact, but for special circumstances in individual localities there would have been a complete cessation of gold mining in Australia during the war. This has been brought about by the uselessness of gold as an industrial metal, the existence of a world-wide barter agreement among the anti-Axis nations which for the time being does not call for gold to balance trade deficiencies, and the need to employ as many men as possible in the most essential work.

It will be seen by reference to the table below that the decision drastically to curtail gold mining has had its most serious effects in Western Australia, where many communities have been established, entirely dependent upon gold mines. The gold mining districts of Victoria, e.g. Bendigo and Castlemaine, have also been hard hit. Other States have not suffered so much because only in very few places in those States are there mines solely devoted to winning gold. For instance 50 per cent. of the Queensland production is from Mount Morgan, which is also important as a source of copper.

AUSTRALIAN GOLD PRODUCTION, 1939.

							Fine Oz.
New South Wales	87,189
Victoria	156,522
Queensland	147,248
South Australia	3,930
Western Australia	1,214,238
Tasmania	19,984
Northern Territory	16,586
Total	1,645,697

It is unnecessary to spend much time discussing *silver*. Ninety per cent. of the silver consumed in Australia is required for coins, 10% is used industrially for such purposes as photographic materials, electroplating, surgical plates. However, no mining operations can now be regarded as being carried on primarily for the recovery of silver. Some silver is obtained with gold, but the bulk of it occurs associated with lead and zinc, both of which metals are required for war purposes. It is of interest to note that 60% of the world consumption of silver is used industrially.

Australian resources of *platinum* and *osmiridium* are small and large production cannot be expected. Annual production of 200-300 ozs. of osmiridium can normally be obtained from alluvial sources in Tasmania. However, this is one kind of production which has been most seriously affected by manpower demands, as I shall indicate later in this address.

FUELS.

Australia possesses adequate supplies of *bituminous coal* for some considerable time to come. These supplies however are not nearly as large as is popularly believed and certainly not large enough to permit our present wasteful methods of mining to continue indefinitely. I speak of course in terms of a generation or two, not of the immediate future.

Figure 1 shows the distribution of coal deposits in Australia. It will be noted that nearly all of them are close to the coast and it will be realised that this distribution has been an important factor in accentuating population distribution in the coastal areas. The principal deposits of bituminous coal are in Queensland and New South Wales. Reserves of coal available in these two States are probably approximately equal.

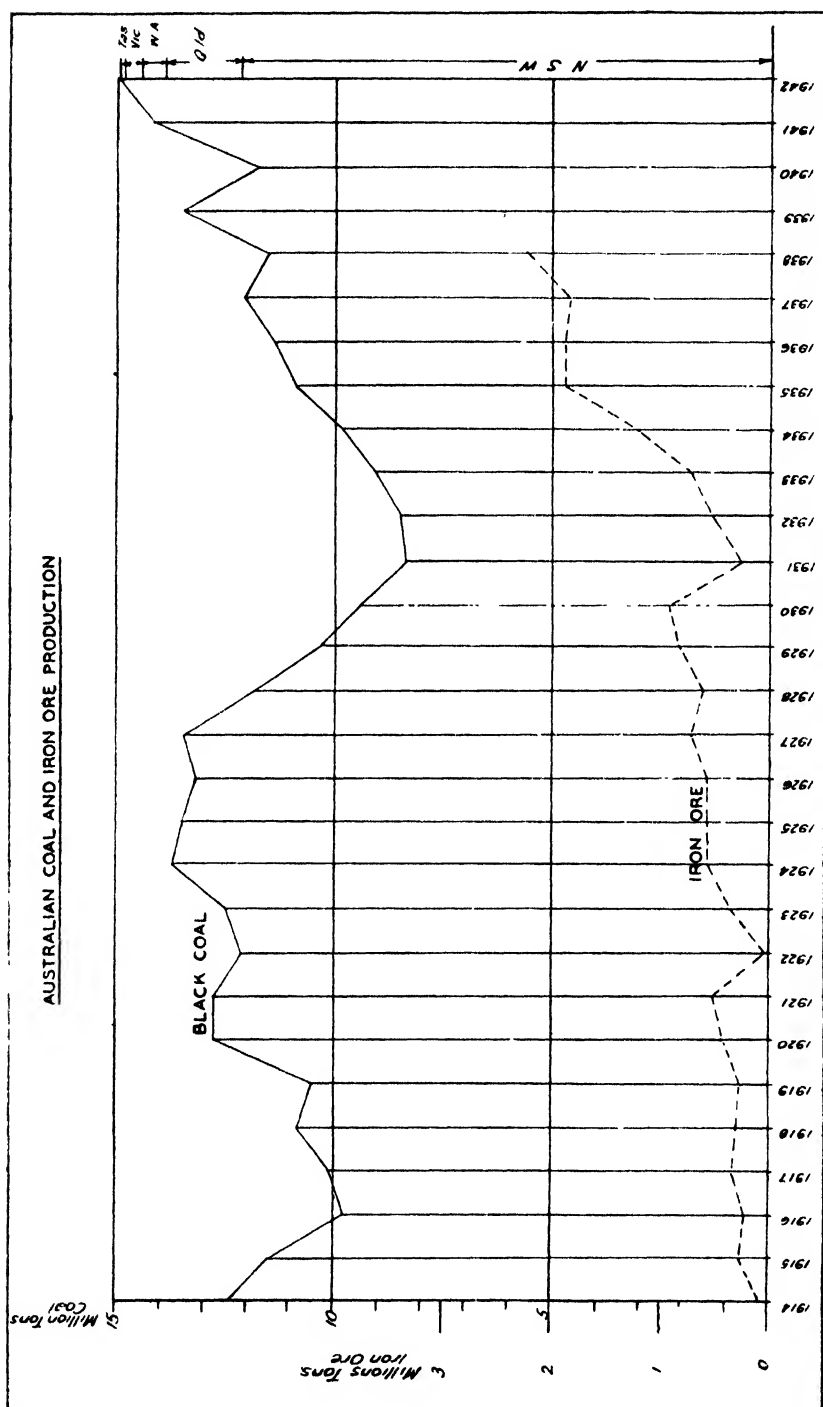


Fig. 2.

Figure 2 shows graphically the production of coal in Australia for the period 1914-1942 and for each of the producing States in 1942. It can readily be seen from this figure that the production and distribution of coal won in New South Wales are the outstanding features of the industry and that transport of coal from New South Wales to the other States has presented a major problem to the responsible authorities. These difficulties have directed attention to the possibility of development of coal deposits considered relatively unimportant in pre-war years, but which, if developed now, would release transport for other purposes.

Victoria is badly off for bituminous coal, but the sub-bituminous coal of Wonthaggi has come in useful in the present emergency. As the geologists present know, this coalfield is a maze of faults which makes mining costly and difficult.

In the hope of releasing transport now engaged in carrying coal from New South Wales to the Riverina and Victoria, attention has recently been directed to the Coorabin-Oaklands coalfield. Supplementing the work done earlier by the New South Wales Mines Department and private interests, a considerable amount of boring has been done on behalf of the Commonwealth Coal Commission. As a result it has been concluded that the field has interesting possibilities but that it could not be brought into production quickly on a scale large enough to be of much assistance in the present emergency.

Tasmania has several areas of bituminous coal, and production has been augmented during the war to meet increased demands. This has been achieved with only slight addition to the labour force engaged. Production in 1942 was 134,442 tons. Importation of New South Wales coal amounting to about 100,000 tons is still required for gas making and special steam raising purposes.

Difficulty in obtaining sufficient supplies of New South Wales coal has forced the South Australian authorities to give attention to the Leigh Creek (Copley) field. Leigh Creek is situated on the North Australian railway 165 miles north of Port Augusta in an area where large supplies of water are difficult to obtain. The coal from this field is a low ranking sub-bituminous type and its industrial application is going to be difficult. However, prospecting of the field has been pursued with great vigour by the South Australian Government and the field is now being developed.

The State of Western Australia has very large areas occupied by sediments of the same geological age as those in which the major coalfields of Queensland and New South Wales occur, but unfortunately in their areas of maximum development, these sediments do not include coal of commercial quality and thickness. The coal produced from the Collie district in the south-west part of the State, however, is a very useful fuel and sufficient is produced to satisfy most of the State's power and transportation requirements.

Even were the resources of black and near-black coal in States other than Queensland and New South Wales fully developed, those States would still require a certain amount of coal from New South Wales or Queensland for gas making and some special steam-raising purposes.

The *lignite* resources of Victoria are too well known to need redescribing. They have been very thoroughly investigated by the Victorian Mines Department and the State Electricity Commission. Total known reserves are very large but much of this is under deep cover. A great State-owned electricity generating station and briquetting factory are based on these deposits at Yallourn.

Considerable reserves of lignite have also been proved in South Australia, but are undeveloped.

A fundamental weakness in the Australian economy is our lack of resources of *liquid fuel* or adequate substitutes therefor. Parenthetically it may be remarked that this weakness goes side by side with lack of large surface water resources for the generation of electric power. Australia has about the same area as the United States (Alaska excluded) and it has been suggested that industrial development of this country comparable with that of the United States can be expected in the post-war years. I am, I hope, a patriot, but when I consider the vast coal, oil and water resources of the U.S.A. and compare them with our own, I know that this cannot be, on the basis of known sources of fuel supply. Broadly our coal and water resources are known and the necessity for making an exhaustive survey of our petroleum possibilities is thus shown to be of paramount importance.

Australia has never had a policy on petroleum exploration, but it will be forced to have one when the war ends. The American technical press is filled with articles pointing out that the discovery rate in that country is much below what is necessary to allow production rates to continue and maintain reserves. Exploration is going on at a rapid rate in South America, especially in Venezuela and Colombia, and after the war there is undoubtedly going to be a search for oil reserves on a scale previously unknown outside the U.S.A. Even areas previously considered, and regarded as unpromising, will be reexamined. Australia will not go unnoticed in this world-wide exploration programme.

Figure 3 shows very broadly the areas considered to offer the best promise for commercial accumulations of oil and gas in Australia and New Guinea.

It must be admitted that, so far, the search for oil in Australia and the nearby islands has been disappointing. It is also true, however, that, with some notable exceptions, it has not been exhaustive. The most intensive studies have been made by private companies, e.g. the Australasian Petroleum Company in New Guinea and Papua, the Shell Company in Queensland, and Caltex (Aust.) Limited in Western Australia. The first of these had reached a stage where boring was in progress when the war began. Some commendable work, involving mapping of large areas, has also been done by the relatively small Australian companies, Oil Search Limited and Freney Kimberley Oil Company.

The search for oil in Australia is now virtually suspended, partly because some of the most promising regions are within a combat area and partly because it is realised that in most of the potentially oil-bearing areas a long programme of survey, prospecting and development is required, and the results could have no bearing on the present conflict. An exception is the Lakes Entrance district in Victoria, where oil has been proved to be present in a glauconitic sandstone (of Middle Miocene age) extending over an area of 8 square miles at an average depth of about 1,200 feet. The proving of this area has been done mainly by small companies, but the State, and State and Commonwealth together have also assisted. Fortunately the area was brought under the control of one company, Austral Oil Drilling Syndicate, in 1940. This syndicate is to be congratulated for its efforts in collecting, collating and preserving all drilling data it was able to acquire. The central section of this area is to be developed by application of the method recommended by Mr. Leo Ranney (1941), which consists in drilling horizontal holes radially from a circular vertical shaft. The sinking of the shaft is in progress under the joint direction of the Commonwealth and Victorian Governments.

The *torbanites* (*kerosene shales*) and *oil shales* of New South Wales, Queensland and Tasmania offer some possibilities of oil production. Interest at present centres in the Glen Davis project which recently formed the subject of a report by the Commonwealth Parliamentary Committee on Public Works. The

following paragraph from that report expresses conclusions concerning this subject with which I agree :

"During the course of its enquiries, it was increasingly borne in on the Committee that this project could not be considered from the ordinary commercial standpoint, but must be regarded from a national point of view. The Committee has formed a definite conclusion that petrol of a satisfactory quality can be produced from Glen Davis shale, but the cost, having regard to the loss of Customs revenue, would be at least twice that of imported petrol. On economic grounds, the establishment of an industry is not warranted, and it could be justified only on the importance for national considerations of developing an Australian oil industry."

Here again Australia needs a national policy with regard to oil. The whole field of possibilities requires to be surveyed and the economics of various proposals contrasted—the different possible sources of oil cannot be properly considered by themselves.

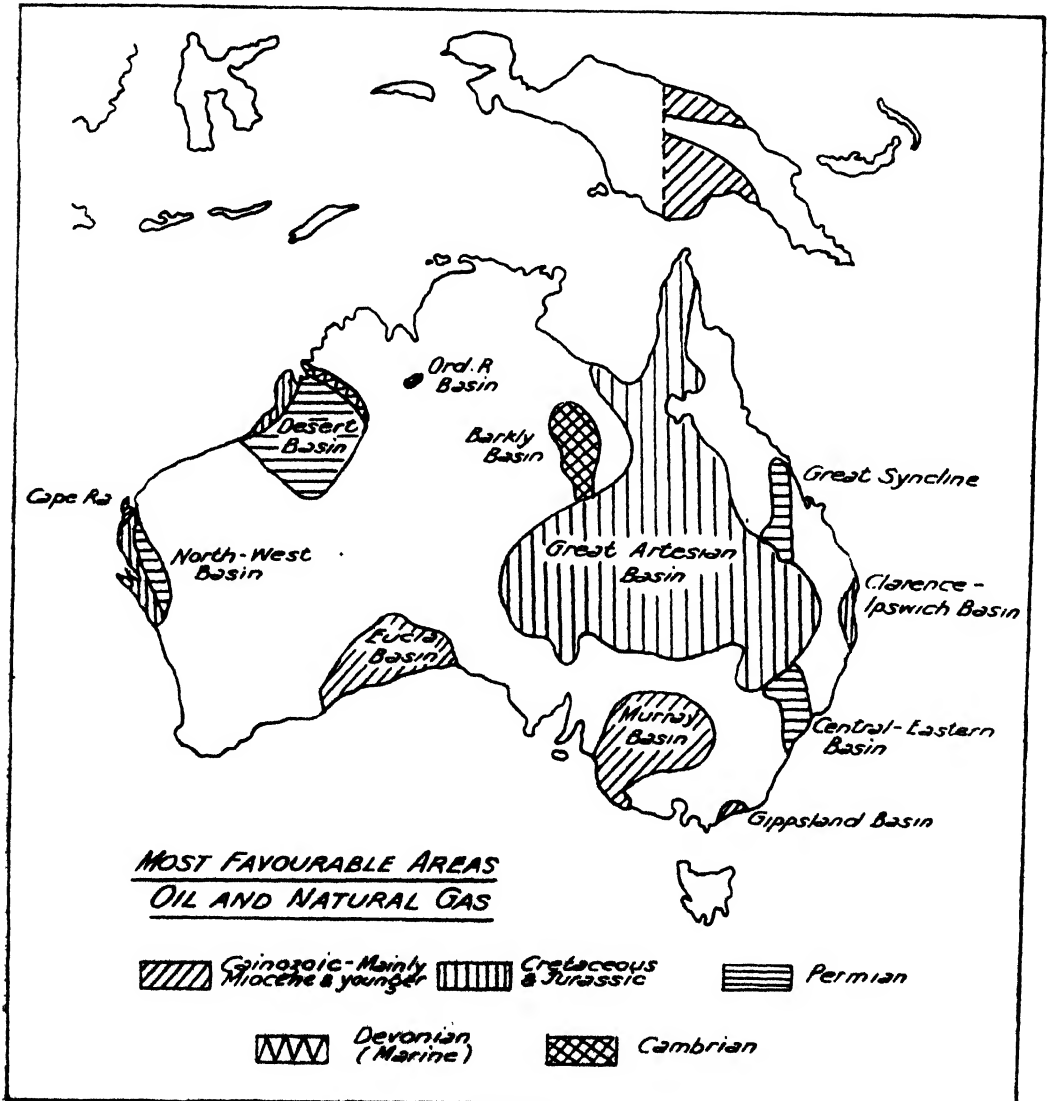


Fig. 3.

Australia never seems to have regarded her *natural gas* possibilities seriously. Preoccupation with the idea of finding petroleum has led many to dismiss gas showings with the phrase "it's only methane", yet natural gas, which is mostly methane, is almost the ideal fuel for many purposes. The main interest attaches to gas supplies near large industrial centres and probably this industry will follow the usual stages. Potential consumers will begin to realise that in natural gas they have a convenient fuel near at hand, and from this beginning its use will spread. It will be realised also, that with proper technique, large supplies of gas can be obtained over long periods from natural reservoirs, thus justifying capital outlay on pipe lines. Some industries will ultimately realise it may be to their advantage to establish themselves near gas supplies.

Regional surveys and reconnaissance drilling for natural gas have been suspended for reasons similar to those mentioned under the heading of petroleum, but an interesting experiment is in progress at the Balmain Colliery, City of Sydney, which has reached a decisive stage.

Here it is interesting to note how the chain of events takes us back to the man we honour tonight, for it was the Rev. W. B. Clarke who first suggested, in 1847, when giving evidence before a Select Committee of the New South Wales Legislative Council, that coal might be found underlying the Sydney district at a considerable depth. Later Sir Edgeworth David became interested in the subject and in the light of the evidence then available forecast the approximate depth at which coal might be expected beneath Sydney. In 1891 the first Cremorne bore (on the north shore of Sydney Harbour) struck coal at approximately 2,802 feet. The sinking of the Cremorne bore was followed by the putting down of the Birthday Shaft at Balmain on the southern shore of the harbour between the years 1897 and 1902.

At the Balmain Colliery, coal has been developed from vertical shafts nearly 3,000 feet deep. From these shafts, workings extend underneath Sydney Harbour. When the colliery was working, the amount of gas liberated per ton of coal mined was 2,500 cubic feet. This is a very high yield. Recent investigation showed that despite the fact that seals placed in the workings when mining ceased in 1931 were broken, and that there was therefore free movement of air through the workings, they were full of gas and even under these conditions the gas had a calorific value of over 900 B.t.u. It was therefore demonstrated that under static conditions a coal face will exude gas for a long time.

Seals have been erected in the colliery so that it will be completely air-tight and methane gas is being extracted from the workings by putting a vacuum on a pipe leading from the workings to the surface. The result of the experiment depends of course upon the length of time during which gas will continue to be given off by the coal face, and the rate of yield. At present 100,000 cubic feet of methane with a calorific value of 960 B.t.u. (equivalent to 1,000 gallons of petrol) is being marketed per week and used as a petrol substitute. The fact that the Balmain colliery is situated within the City of Sydney and that marketing of large quantities of gas will present no difficulty, made this experiment especially well worth doing. It is to be hoped that if the experiment is successful other similar prospects will be brought into production.

At a later date it is hoped that Mr. Leo Ranney's (1941) scheme of degasifying the coal in the Balmain colliery will be tried. This scheme has two objects: to produce methane gas for use as such, and to degasify the coal and so make working conditions safer.

I should like to see our coal-mining engineers pay more attention to degasification as well as to gasification of coal seams *in situ*, a method apparently now widely practised in Russia.

IRON AND STEEL.

You all know that our iron and steel industry is based chiefly upon coal produced in central-eastern New South Wales and iron ore produced from the Middleback Ranges in South Australia. Due to the difficulties of maintaining shipments of coal and iron between these points it has been found necessary to draw upon the many somewhat small deposits in New South Wales. Cadia, Crookwell, Breadalbane, Tirranna and Michelago are some of the centres from which supplies are being drawn to help keep up Australia's output of steel.

There is a lesson to be learned here, namely that the value of a natural resource is not a static thing; geographic position and changing circumstances may be, and often are, more important than any intrinsic worth the resource itself may possess. Some people were inclined to scoff at the re-surveys of New South Wales iron ore resources made in the years immediately preceding the war. But this audience would be surprised if I could say what proportion of Australia's steel requirements are being met from sources in New South Wales. Surveys of mineral resources should therefore be comprehensive, thorough and continually subject to revision.

Steel is the basic metal in war and, fortunately, far-sighted men have seen to it that Australia has a strong and efficient steel industry. Without this, our munitions effort could not have been made. It was only in 1915 that the B.H.P. Steel Works were opened. "Today, Australia can produce steel more cheaply than either Great Britain or the U.S.A. Within the short period of twenty-five years Australia has become self-sufficient in steel. Her production *per capita* is roughly equal to that of Great Britain and more than double that of Japan. Only Germany and U.S.A. can claim a higher *per capita* production." These words are taken from a recent statement by Mr. H. G. Darling (1943), Chairman of Directors of B.H.P., who himself has played no mean part in this modern miracle and who regards the future of the Australian steel industry with unshakeable confidence. We would do well to note the basic economic factor to which Mr. Darling attributes our success in steel making, namely, the ready availability of coal and iron ore at or near tidewater.

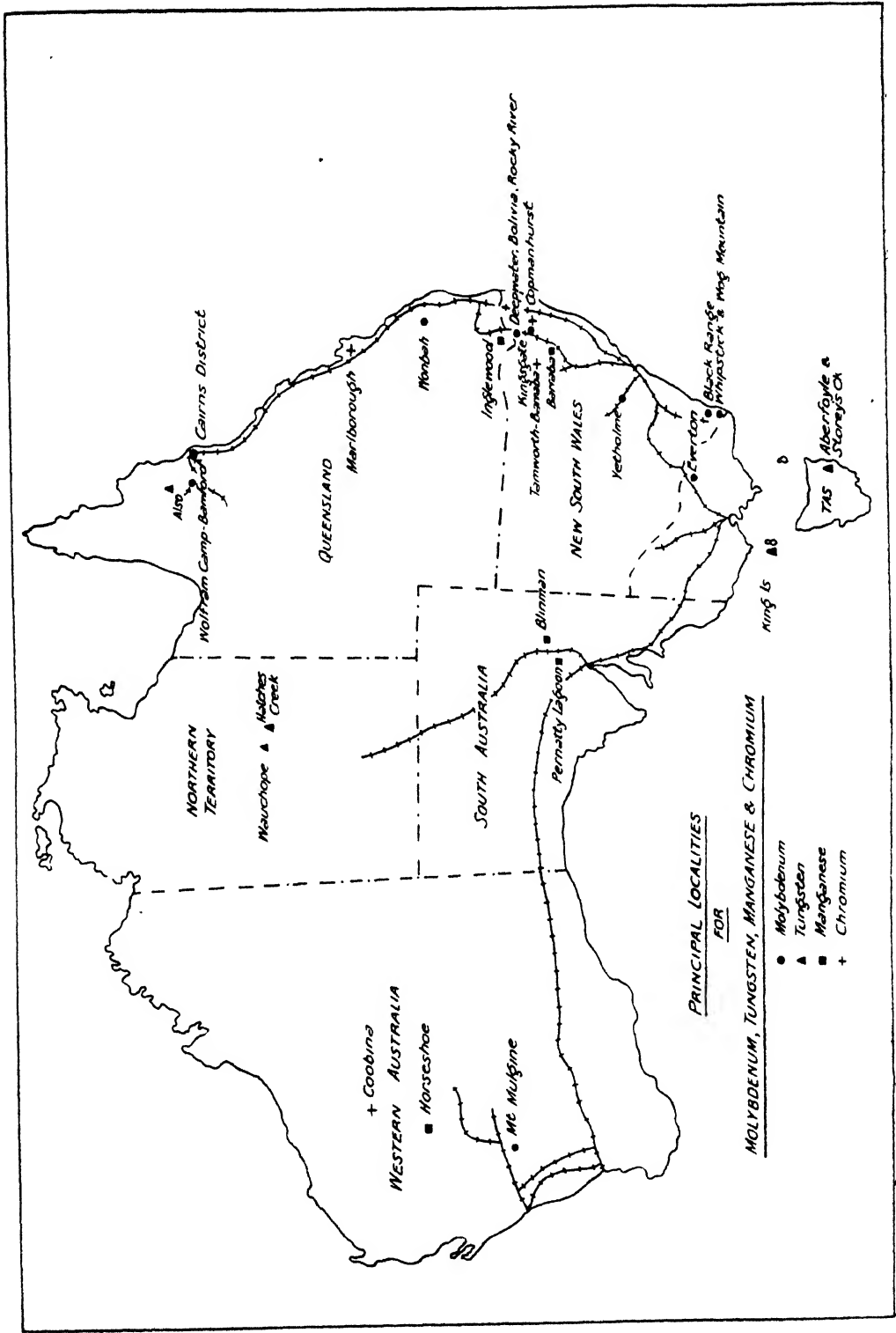
The very close relationship which exists between coal and steel production is shown by Figure 2, which also gives the production of iron ore in Australia for the period 1914-1938. The publication of later figures is not permitted.

FERRO-ALLOYS.

In discussing coal, other fuels, and iron ore we have been dealing with commodities which, unless they occur in large quantities, are almost valueless. They are both also so essential to modern industry in times of peace, no less than in war, that the State and private interests have made it their business to investigate available resources. The same remarks do not apply to the ferro-alloys. The annual production of some ferro-alloy metals might reach only a hundred tons and still be a very valuable contribution to the war effort.

The outstandingly important metals of the ferro-alloy group are tungsten, molybdenum, manganese, chromium. The principal localities for these metals in Australia are shown in Figure 4. Nearly all the deposits of the first three of these metals in Australia are of the vein or pipe type which do not lend themselves to large-scale production. Most of the chromium deposits are small and irregular. Hence production curves for these metals show sharp fluctuations, the peaks representing discoveries of easily worked deposits, soon depleted, plus a response to the stimulus of high prices ruling in the last war. (See Figures 5 and 6.)

There are exceptions to the foregoing generalisation including the scheelite deposit at King Island, the deposits of *manganese* at Pernatty Lagoon, South Australia, and the well-known deposits of manganese at Horseshoe, and *chromite* at Coobina, Western Australia. Both the latter constitute a valuable reserve



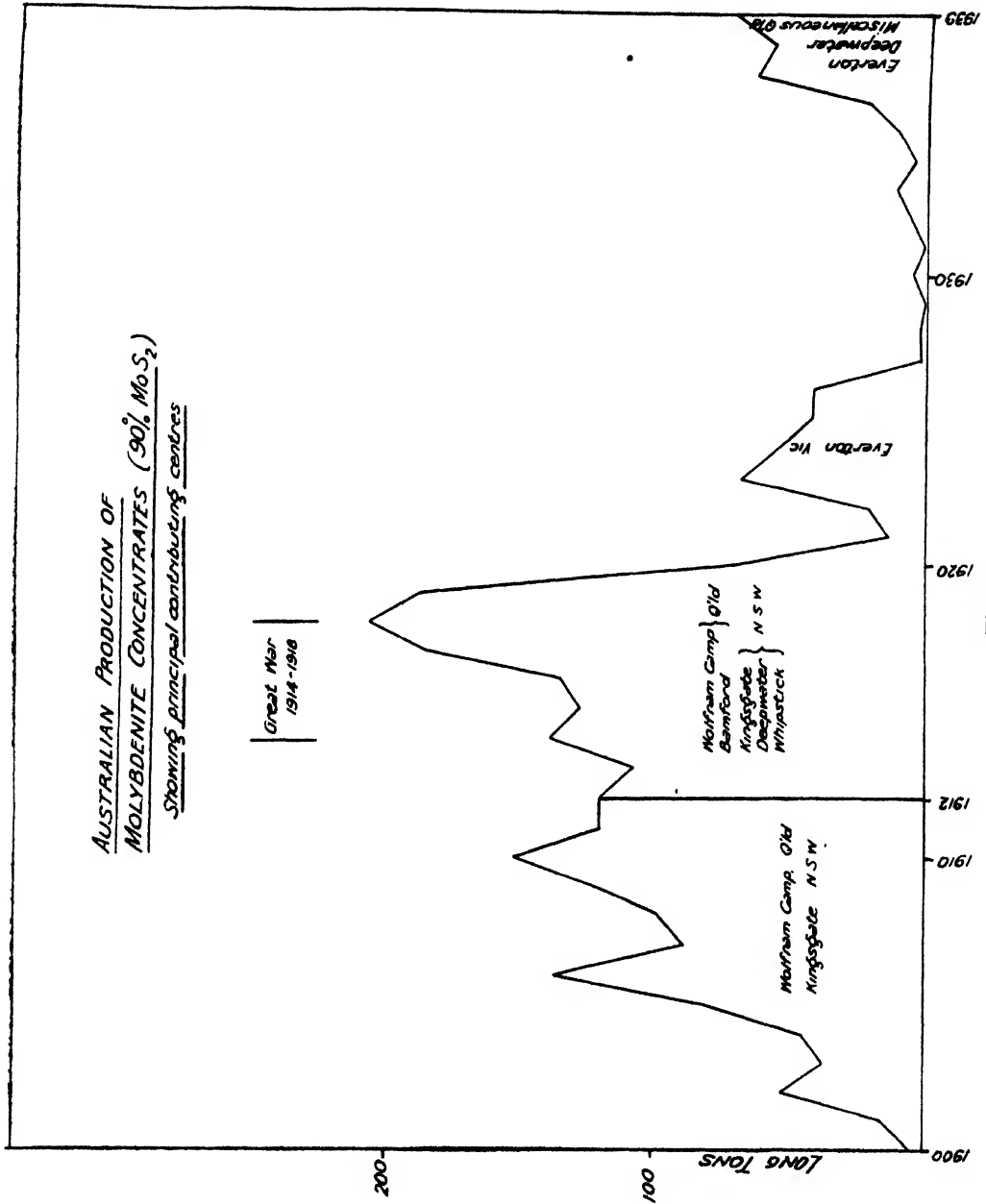


Fig. 5.

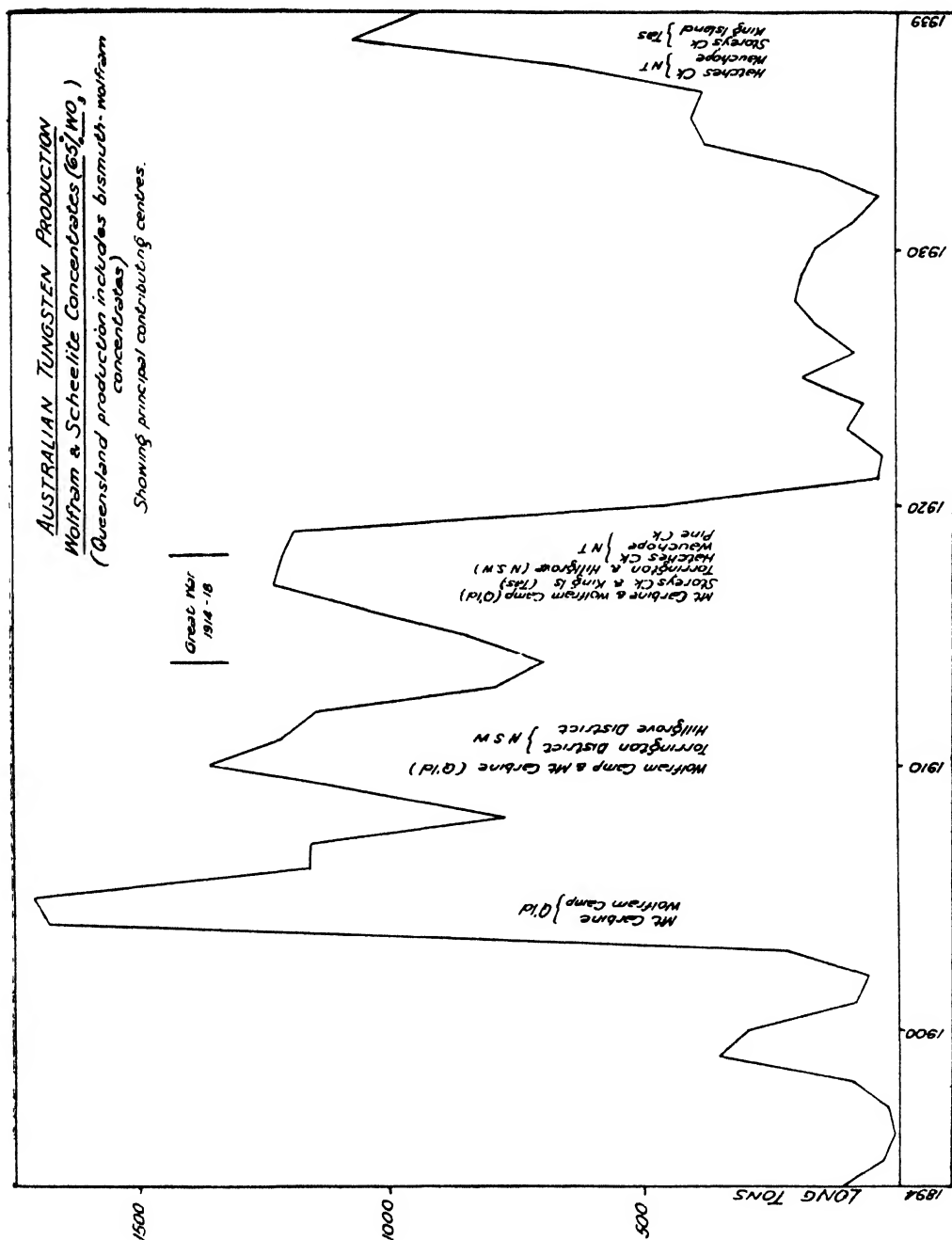


Fig. 6.

but have not been worked, chiefly because of the high transport costs involved and because sufficient high-grade chrome ore has continued to be available from New Caledonia, and sufficient manganese ore for metallurgical purposes has been available until recently from Pernatty Lagoon. It is now believed the latter deposit is virtually exhausted and it has therefore been necessary recently to import ore for metallurgical purposes.

When the war began it was thought unlikely that we would be able to obtain within Australia adequate supplies of high-grade manganese ore (pyrolusite) suitable for use in dry batteries. There are no large deposits of ore suitable for this purpose known to exist in Australia, but it now seems possible that sufficient ore will be available from a number of small deposits in Papua, Queensland and New South Wales to meet requirements. Recent work by the Ore-Dressing Laboratory of the New South Wales Mines Department suggests that simple methods of beneficiation can be applied to ores mined in the Tamworth district (which are known to be suitable for use in batteries but which are somewhat low in MnO_2 content) and perhaps also to similar ore from northern Queensland. Papuan ore is satisfactory without treatment but the ore bodies are believed to be small and mining and transport difficulties are of course difficult to overcome at the present time.

High prices and a strong demand have had little effect upon production of molybdenite, the ore of *molybdenum*, and no really large sources of supply are known. Production is increasing, however, and the deposits now being developed at Wonbah in Queensland, Whipstick in New South Wales and Everton in Victoria should provide useful increments to output in the near future. Though very large supplies of molybdenite are available in the United States they are not sufficient to meet all requirements of the Allied Nations.

By overrunning part of China, Thailand and Malaya the Japanese obtained access to abundant supplies of wolfram, and thus effectively cut off the allied nations from access to the principal sources of *tungsten* ore. In 1939 world production of tungsten concentrates was about 33,000 tons, of which 60% came from China and adjacent lands, 10% each from Portugal, Bolivia and the United States, and 3% from Australia and Argentina. As tungsten is an absolutely essential metal for war purposes, a special effort on the part of all allied nations was obviously required.

The maximum production of tungsten concentrates from Australia was obtained in 1905 when about 1,700 tons were produced, nearly all of it in Queensland. In 1917 and 1918 production fell just short of 1,100 tons. It will be apparent, therefore, that early in the war the prospects of really large production of tungsten concentrates from Australia were not hopeful but the outlook has been completely changed by the results of a diamond drilling campaign on King Island, Tasmania, completed a few months ago. This was done on the recommendation of the Minerals Committee following a report by Messrs. Mawby and Nye. The King Island deposit is now shown to be one of the largest of its kind in the world. It can, moreover, be developed by open cut methods and everything is now being done to increase output. It is greatly to be regretted that the size of this deposit was not realised earlier, but there is no blame attaching to anyone for that. The deposit is a disseminated type and its size could only be determined by a costly diamond drilling campaign. The planning of the development is the responsibility of the Controller of Minerals Production, acting as adviser to the King Island Scheelite Company. This seems to be a case where "Government interference" has had useful results.

Until full-scale development is reached at King Island, requirements must be met by existing production from that source and other smaller ones, chief of which are the Aberfoyle and Storey's Creek mines in Tasmania, the Hatches Creek and Wauchope Creek fields in the Northern Territory and the Wolfram

Camp area in Queensland. There are, of course, many other small producers, most of them in eastern Australia.

As virtually all the *bismuth* currently produced in Australia is obtained as a by-product from the mining of tungsten and molybdenum, it may be conveniently mentioned here. By making a special effort Australia could just about attain self-sufficiency in bismuth, but it is impossible even to consider making such an effort whilst manpower requirements for other vital production are unobtainable.

BASE METALS OTHER THAN IRON.

The principal metals dealt with under this heading are lead, zinc, copper and tin. The principal producing centres are shown in Figure 7. As all current production of cadmium and cobalt in Australia is obtained as a by-product from the treatment of zinc concentrates those two metals are also dealt with in this section. Lead, zinc and copper are all required in large quantities, the first three chiefly in direct munitions uses.

Tin. The main uses of tin are in tinplate, solder and bearing alloys. Thus in normal times tin production is closely linked with that of steel. If necessary war could be waged without tin. Germany managed to do this in the first world war but only with special effort in other directions and at considerable inconvenience. One can imagine what difficulty we should have keeping up supplies of food and other commodities to the fighting forces if a substitute had to be developed for tinplate.

The overrunning of Malaya and Burma by the Japanese and their blockade of China cut off the allied nations from large supplies of zinc and tin. Of the estimated tin content of ores produced in 1940 (231,700 tons) 70% (160,687 tons) came from the Malay States, N.E.I., Siam, China, Burma and Indo-China. It must also be remembered that nearly 60% of the world's production of tin was smelted in this region.

That this position might arise had been anticipated to some extent and stocks had been built up. Steps had also been taken to increase smelter capacity, especially in the U.S.A., where arrangements were made to handle Bolivian concentrates.

In the period 1873-1882 (except for two years) Australia held first place among tin-producing countries. Her production was approximately 11,500 tons per annum, representing 25% of the world total. In 1939 Australia's production was approximately 3,600 tons. Naturally everything possible has been done to increase output since that year and rationing has been applied to civil uses.

Tin is produced in Australia from both veins and alluvial deposits and production is about equally divided between Queensland, New South Wales and Tasmania. Since much of the tinstone won in Queensland and New South Wales is obtained by a large number of small producers, factors to which I shall refer in closing this address, have had most serious effects on output. Fortunately these are gradually being overcome and good progress has been made in bringing new production into effect. The Tableland Tin Company's dredge is now operating in the Mount Garnet district, Queensland and is expected to produce at the rate of 1,000 tons of metal per annum. A dredge is also being assembled on the Dorset Flats in north-east Tasmania and increases may also be expected from some of the regular producers. (It is interesting to note here that the dredge at Dorset Flats has been taken from a former gold-producing property.) Just as we have been very fortunate in having a scheelite deposit of the magnitude of King Island so it seems fortunate that the Mount Garnet area in northern Queensland is commencing production at a rate which will relieve any anxiety with regard to tin supplies in Australia and allow some

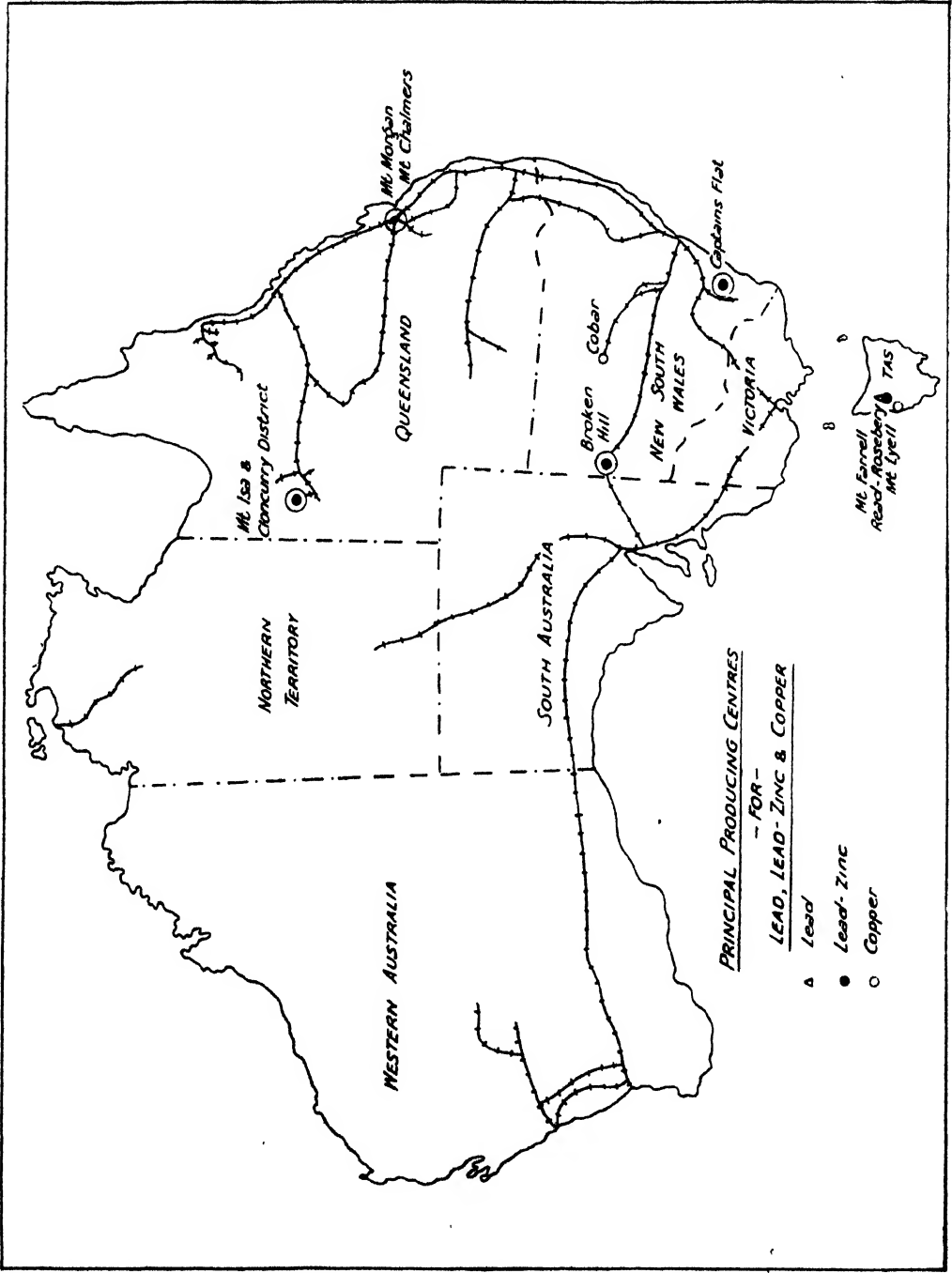


Fig. 7.

export. A most remarkable development has also occurred in the copper industry to which reference will be made shortly.

Copper. It may come as a surprise to many who remember the old copper mines of South Australia, northern Queensland and central New South Wales, that Australian production of copper is far below consumption. This, of course, is largely a reflex of our greatly expanded munitions projects.

It will be of value to refer to a table giving production of copper in Australia in 1939 :

								Tons.
Queensland :								
Mount Morgan	3,300	
Cloncurry District		2,083	
New South Wales :								
Broken Hill..	883	
New Cobar Mine		515	
Captain's Flat	484	
Tasmania : Mt. Lyell	13,483	
All others (mainly Queensland)		549	
Total	20,718	

From this table it will be seen that the number of mines which made noteworthy contributions to Australian copper production in 1939 were few and that Mt. Lyell was easily the largest source. It may be noted incidentally that Mt. Lyell reserves are nearly 15 million tons of 1.14% ore.

This year the story will be very different, due to developments at Mount Isa. Production of copper (metal) commenced at this mine in April, 1943, and it is estimated that by the end of the year the monthly production will be approximately equal to that of Mount Lyell. Proved reserves at Mount Isa amount to 1½ million tons of 3% ore, but the limits of the orebody have yet to be defined.

The Mount Isa mine is known as a large producer of lead, zinc and silver and it must be considered very fortunate that two large orebodies should exist side by side in such a way as to enable them to be developed from the one set of main workings. It is further remarkable that the one orebody contains little copper and the other no lead or zinc. The copper-body is also free from other deleterious metals so that much of the copper produced will probably not require electrolytic refining, but can go into industry as "fire-refined". The Mount Isa copper lode does not outcrop. It was discovered by diamond drilling into the hanging wall of the lead-zinc orebody and has been outlined from level to level by this means. The relationship of the two orebodies is shown in Figure 8, which is slightly amended after Figure 6 of a paper by Blanchard and Hall (1942). This amendment has kindly been made by the authors.

The production of copper at Mount Isa has only been achieved at the expense of that of lead and zinc (because of manpower difficulties) and it has not been possible to man the other copper mines in the district.

Another interesting wartime development relates to changes in smelter practice at Port Pirie. Before the war, the amount of lead present in copper matte received at Port Kembla from Port Pirie governed the amount of lead-bearing copper matte and concentrates Port Kembla could accept for treatment. One effect of this was, for instance, that copper produced from Captain's Flat was lost to Australian consumers. Improved smelter procedure at Port Pirie however has changed all that. Port Kembla can now not only take the whole of Captain's Flat's production of copper concentrates, but copper-bearing ore from Mount Gunson, South Australia, has gone to Port Pirie in place of barren sandstone flux, and Read-Rosebery mines are enabled to mine ore containing a

higher percentage of copper than was formerly possible. This must be acclaimed a noteworthy and opportune technical achievement.

Lead and Zinc. Earlier I referred to the loss of zinc occasioned by the Japanese overrunning Burma. The extent of this loss may be realised from the

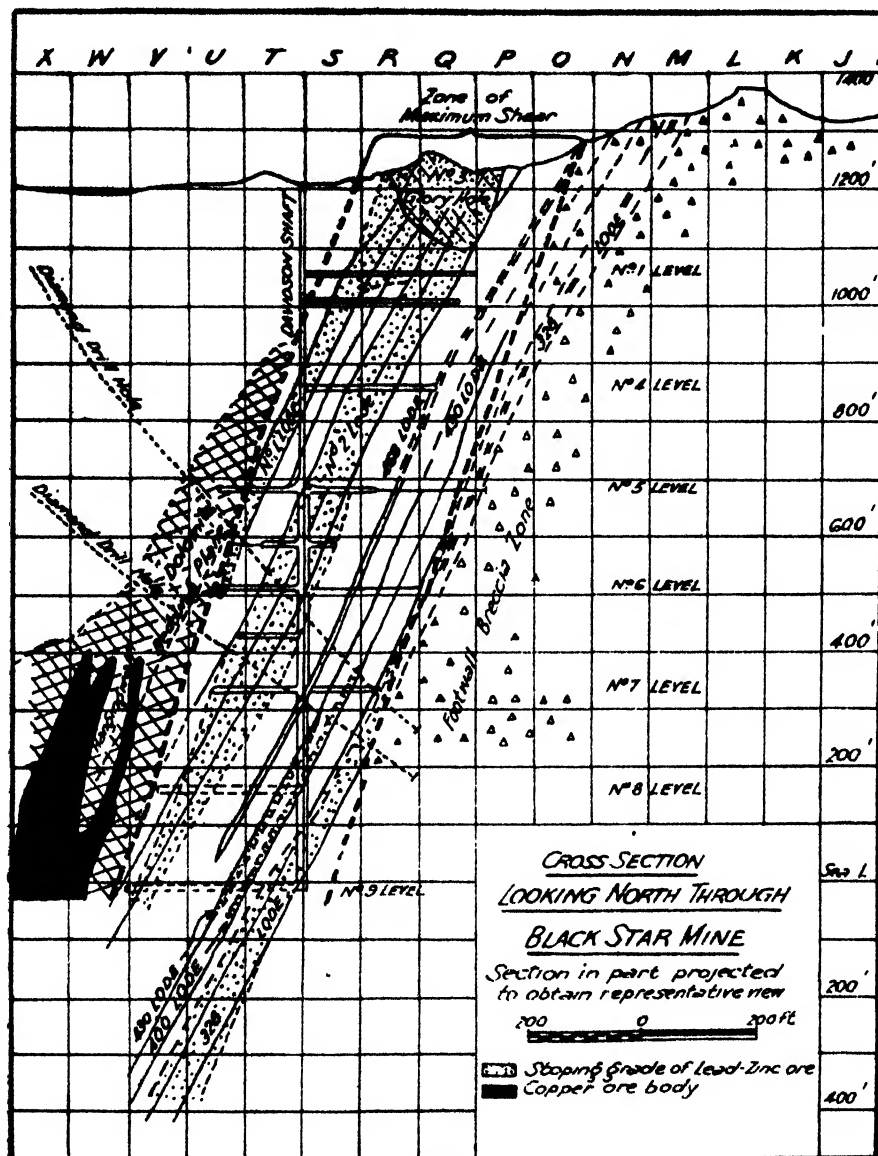


Fig. 8.

fact that Burma Corporation Limited, operating the Baldwin mines, produced 59,500 tons of concentrates in 1939, i.e. twice the normal annual production from Mount Isa mines.

Fortunately, contributions of lead and zinc which Australia can make to the united nations war effort are considerable, but as production comes from a few well established mines, little discussion is required. The most important producing centres of lead and zinc are Broken Hill district and Captain's Flat in New South Wales, Mount Isa mines in Queensland and the Read-Rosebery

mines in Tasmania. In addition approximately 2,500 tons of lead are produced from Mount Farrell in Tasmania. The relative importance of these centres may be gauged from the following production figures for the year 1939 :

	Lead.	Zinc.
Mount Isa	45,265	29,041
Broken Hill	204,692	145,434
Captain's Flat	7,145	11,425
Read-Rosebery	8,515	25,021
Mount Farrell	2,365	—

It has already been pointed out that, because of the greater necessity to produce copper for home consumption it has been necessary to divert men from the production of lead and zinc at Mount Isa to copper, but the output of lead and zinc from the other three main centres is still very considerable. In fact, despite all difficulties, production of both metals is above the previous record levels which were realised immediately prior to the first world war. If a special effort were needed to increase production of either or both of these metals, the only essential requirement is additional manpower, as reserves and all the necessary facilities for mining and treatment exist.

The Broken Hill orebody besides yielding large quantities of silver, antimony, copper, lead, zinc and gold, is also our only present source of *cadmium* and our main source of *cobalt*. Both these metals are recovered in the Electrolytic Zinc Company's plant at Risdon, Tasmania. Cadmium is required mainly for electroplating and the manufacture of bearings. Cobalt has many uses, perhaps chiefly as metal, in cutting tools, dies, etc., as oxide in ceramics and in the form of cobalt salts as driers in paints and varnishes.

LIGHT METALS.

The most important of these metals are aluminium and magnesium, but beryl (the ore of beryllium) and lithium minerals may be conveniently referred to under this heading.

Magnesium is produced by the B.H.P. at its Newcastle works. Magnesite mined in New South Wales is used and the metal is produced by thermal reduction of calcined magnesite with calcium carbide. Though production commenced only in 1941, for a time some metallic magnesium was exported to Great Britain, but this has now ceased due to the increase in our own consumption. Substantial quantities of calcined magnesite have, however, gone forward from New South Wales to the United Kingdom. Australian reserves of magnesite are fairly large, the principal deposits being situated in New South Wales, South Australia and Western Australia, and there are also large deposits of dolomite available in Queensland, New South Wales, Tasmania and South Australia. In Britain and U.S.A. substantial quantities of magnesium are made from sea water.

It is most unfortunate that the manufacture of *aluminium* had not been commenced in Australia prior to the war. At that time, however, New South Wales was the only State which had made a survey of its resources of *bauxite*, the principal ore of aluminium. At that time, also, the specification for bauxite suitable for use in the Bayer process, the most widely used method of producing alumina from bauxite was stated to be very rigid. Today it is admitted that bauxite containing not less than 50% alumina and slightly more than 7% silica can be classed as high-grade and bauxites containing only 30-45% alumina and 30-45% silica plus ferric oxide are included in the estimate of reserves given by the United States Bureau of Mines. Great stress was also laid upon the cheap electric current available in the principal producing countries. In those days the overall costs borne by the aluminium industry in Canada and U.S.A. were apt to be forgotten. It would be wise to remember them today.

Canada, one of the great aluminium producing countries of the world, has no bauxite deposits of any consequence and reserves of high-grade bauxite in the U.S.A. are insignificant. Nearly all the aluminium produced in both these countries is made from bauxite imported from British and Dutch Guiana. It is believed that all this ore occurs beneath overburden and that it is crushed, washed and dried before shipment. Much of the bauxite thus imported into U.S.A. is converted to alumina at New Orleans and Mobile—and from those points is sent to various parts of the United States where the larger supplies of electricity are available for reducing the alumina to metal. Some alumina is shipped via the Panama Canal as far as Vancouver.

With this picture of the American industry in mind we may consider our own major bauxite resources. (See Figure 9.)

In eastern New South Wales there are proved reserves of 15 million tons of bauxite containing from 34% to 45% alumina and from 1.76% to 5.47% silica. The deposits occur in two main groups, Emmaville-Inverell and Bundanoon-Wingello, the former being the higher grade. All the deposits are easily accessible and have little or no overburden. Though somewhat lower in grade, the Bundanoon deposits might be preferred to the others because of their nearness to black coal (which is required in the ratio of 1 ton to 1 ton of alumina), fabricating plants and shipping facilities.

Victoria possesses the highest grade bauxite in Australia. Formerly believed to be very small, the reserves are now known to be considerable. For this development our thanks must go chiefly to Sulphates Pty. Limited. It is this company which has discovered most of the bauxite deposits and these discoveries are continuing. A considerable amount of test boring and shaft sinking has been done by the company. The Victorian Mines Department has one of its boring plants operating in the Boolarra district and two deposits near Mirboo North have recently been tested by the Controller of Minerals Production on the recommendation of the Minerals Committee. As a result, proved reserves are now known to exceed 650,000 tons. Of this amount 500,000 tons are known to average about 52% alumina and 5% silica. Details concerning the remainder are not yet available. This ore is readily amenable to simple methods of beneficiation, if this were considered necessary. The main deposits are situated in the Mirboo-North Boolarra district, 80 miles E.S.E. of Melbourne and 20 miles by air line S.S.W. from the State Electricity Undertaking at Yallourn. All are easily accessible. The largest individual lens of bauxite so far discovered in Victoria contains about 200,000 tons. The ratio of overburden (chiefly sands with some clay and lignite) to ore is somewhat less than 4 to 1. The discoveries so far made by no means exhaust the possibilities of this one district, so that it cannot be doubted that the total reserves available in South Gippsland must be fairly considerable.

It is beyond the scope of this address to discuss the origin of Australian bauxites, but this is a most fascinating study. It will interest the geologists to know, however, that the boring above referred to has definitely established the geological horizon of the Gippsland bauxite. It lies on an erosion surface cut out of the older basalt, has itself been eroded and is, in turn, overlain by lignites which can be correlated, both by the ordinary methods of stratigraphy and by foraminiferal content with the lignites worked at Yallourn.

Bauxite was not discovered in Tasmania until late in 1941. The original discovery was made in the Ouse Valley, and though other discoveries have since been made, the Ouse bauxite has turned out to be the highest grade so far known in Tasmania. An area two miles N.N.W. from the village of Ouse, selected by the Tasmanian Department of Mines for testing has been proved to contain 500,000 tons of bauxite with 41.2% "free" alumina and 3.2% silica. The average thickness of bauxite and overburden are respectively $8\frac{1}{2}$ and $3\frac{1}{2}$ feet.

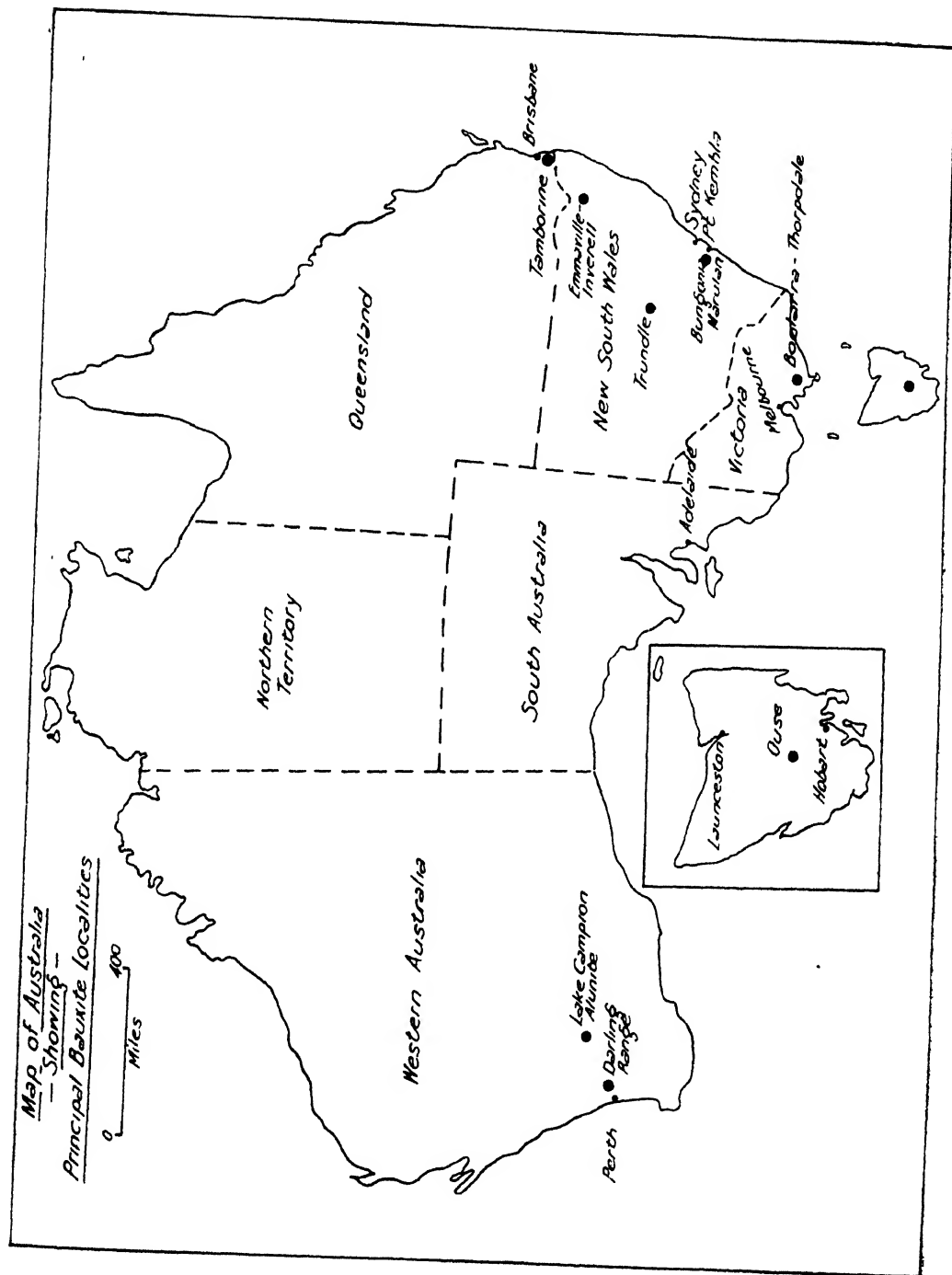


Fig. 9.

The deposits are conveniently situated near coal, water and hydro-electric supplies.

I have very briefly reviewed the general setting of Australia's main known higher grade resources of bauxite. I think you will agree that the general setting is very favourable and that there seems no reason why Australia should not be able to produce aluminium at a price at least equal to that at which it can be imported. You may ask what this has to do with the subject of my address. For answer I would say that our near escape from blockade, if not invasion, ought to point the moral of a country dependent mainly upon air power for its defence depending upon sea-borne traffic for its supplies of the metal with which aeroplanes are built. And further, the faith and industry of a very few people have been responsible for building up the favourable economic picture we now have, chiefly during the war years. It is pleasing to note therefore that the Commonwealth Government has decided to allocate £3,000,000 for the establishment of the ingot aluminium industry in Australia.

My Western Australian friends will say that all this insistence upon the eastern States' bauxite is unfair to their claims for *alunite*. That is not so. Nearly all the world's aluminium is made from bauxite, and that is the only basis upon which a comparison such as I have made is possible. The Lake Campion alunite deposit is an unusual type. Most of the world's alunite deposits are vein-like, and the limited reserves, costs of mining, apart from the difficulties in treatment compared with bauxite, have made them relatively unattractive as a source of aluminium. The Lake Campion deposit, however, is very different. It is a lake filling containing not less than 2 and probably more than 10 million tons of alunite mud. The alunite content of the mud is approximately 60%. A plant has been erected for the recovery of a product containing 75% sulphate of potash and 25% sulphate of soda at the rate of 5,000 tons per annum and it is hoped to expand this production over a period of years to meet Australia's requirements.

The residues from the potash plant will contain about 46% alumina and 37% silica. A pilot plant is being erected (which will make use of acids generated in the potash plant) with the object of finding out whether alumina suitable for the manufacture of aluminium can be prepared from this residue.

Considerable interest has been shown recently in *beryl*, the only ore of beryllium. This has been chiefly for export to the United States, where demand has risen sharply, though the B.H.P. Company has also been anxious to obtain supplies. Beryllium is used mainly in alloys (chiefly in beryllium copper), but it has a number of interesting properties which suggest many possible industrial applications. Beryl usually occurs as a constituent of pegmatite dykes with mica and felspar and some production is sure to result as a by-product of mica mining in Western Australia. Curiously, beryl is rather rare in the mica pegmatites of the Harts Range, central Australia. A relatively large mass of beryl occurs closely associated with the tantalite deposit at Wodgina and the major domestic production is expected from that source. There is some production also from the Mount Isa district in Queensland.

I refer only briefly to the lithium minerals *spodumene*, *amblygonite* and *lepidolite*. There has been some enquiry from America during the past twelve months, especially for spodumene, and the question of producing this mineral from spodumene-pegmatites in Western Australia has been considered. Spodumene could be produced from such sources, but at high cost.

ANTIMONY AND ARSENIC.

Antimony and arsenic may be conveniently dealt with together because, in recent years, the bulk of Australia's production (apart from antimony recovered from Broken Hill ores) has been produced from mines in the Wiluna district,

W.A. After this year, however, the picture will change materially as the antimonial bodies at Wiluna will have been worked out. Probably you are all familiar with the other sources of supply—relatively small stibnite-bearing veins found in many parts of eastern Australia. Antimony in the Broken Hill concentrates is recovered as antimonial lead. Australia is self sufficient in antimony and is an exporter of arsenic, but it may be noted that half the world's pre-war production of antimony came from China and adjacent countries.

Arsenical compounds are required for a variety of commercial uses, and will become important if poison-gas is used as a war weapon. As world production of white arsenic was a record in 1940 it may be inferred that the use of gas is in some people's thoughts. The principal sources of supply of arsenical ores apart from Wiluna are situated near the Queensland-New South Wales border. Several of them were worked when arsenical sprays were being used in large quantities for control of prickly pear.

TANTALUM AND COLUMBIUM.

Tantalum and columbium are both important war metals, the former more particularly. Columbium is used chiefly as ferro-columbium but tantalum is used chiefly as tantalum-tungsten and tantalum-nickel (in radio tubes) and as carbide in dies, steel cutting tools and wear-resistant parts of machinery. The ores, tantalite and columbite are rarely found pure. It is for this reason that the columbium-free tantalite from Wodgina, Western Australia, and the tantalum-free columbite from Nigeria are much preferred to ores from any other source. A special effort is being made under the direction of the Controller of Minerals Production to develop the Wodgina deposit in Western Australia both for tantalite and beryl. It is anticipated that small parcels of tantalite will also be produced from other localities in Western Australia and the Northern Territory and possibly Queensland.

BEACH SAND MINERALS.

I here depart somewhat from the plan of my address to refer to the interesting and important beach sand industry which has developed along our east coast. In time past, gold and platinum were recovered from alluvial deposits behind the modern beaches and the existence of other minerals has been known for a long time. However, it is only comparatively recently that the heavy minerals present in the beach sands have been exploited.

The combined action of streams, which bring the minerals down to the sea, and of waves has built up considerable deposits of sands, chiefly adjacent to the Queensland-New South Wales border. The principal minerals of economic value present in these sands are zircon, rutile, ilmenite and monazite. Garnet is also present, but no commercial use has been found for it so far. Because it contains a small amount of chromic oxide, the ilmenite also has limited use. The problem has been, therefore, first to delineate the areas where the best accumulations of naturally concentrated sands occur, and second, to evolve a method of treatment to yield as clean concentrates as possible of zircon, rutile and monazite. The treatment problem is not particularly difficult and has been solved by the application of tabling, flotation and electro-magnetic separation.

There is a growing consumption of zircon and rutile within Australia. The bulk of the production, however, is exported to the United States of America.

Most of the zircon is used both at home and abroad in the manufacture of ferro-silicon-zirconium with minor amounts in enamel ware, spark plugs, and electrical appliances. The rutile and rutile-ilmenite mixed concentrates, on the other hand, are used mainly for welding rod coatings and secondarily for

ferro-titanium. The manufacture in Australia of flints (ferrocium) using monazite has commenced or is about to commence.

So far this industry has met all the demands made upon it.

SULPHUR, SULPHIDES AND SULPHURIC ACID ; PHOSPHATE ROCK.

A most important aspect of our mining industry is that concerned with the production of sulphuric acid and sulphur, from raw materials available in Australia.

Australia normally obtains its supplies of sulphur from imports of native sulphur (recently almost wholly from U.S.A.), roasting of sulphides (pyrite-marcasite and sphalerite-marmatite), and spent oxide from gas plants (about 300 tons sulphur per annum). The amounts consumed in recent years up to 30th June, 1939 (excluding that from gas plants), are given hereunder.

AUSTRALIAN CONSUMPTION OF SULPHUR.

Year.	Imported Sulphur.		In Home Produced Sulphides. Tons.	Total Tons.
	Tons.	£ Sterling.		
1932-33	93,445	555,844	25,692	119,137
1933-34	67,091	320,262	26,639	93,730
1934-35	63,756	273,349	28,239	91,995
1935-36	106,763	464,644	41,268	148,030
1936-37	90,394	376,383	37,784	128,177
1937-38	141,796	582,499	46,190	187,980
1938-39	115,100	491,212	48,653	163,753

The following table shows that the bulk of the sulphur is used in the manufacture of chemical fertilisers. It is, in fact, used in the manufacture of sulphuric acid, which in turn is used to make superphosphate.

USE OF IMPORTED SULPHUR IN AUSTRALIA (BY INDUSTRIES).

	Chemical Fertilisers.		Chemical, Drugs and Medicines.		Imports. (Tons.)
	Amount. (Tons.)	Proportion of Total. (Per cent.)	Amount. (Tons.)	Proportion of Total. (Per cent.)	
1937-38 ..	104,865	83.4	20,895	16.6	141,796
1938-39 ..	95,701	82.8	19,849	17.2	115,100
1939-40 ..	72,561	81.3	16,695	18.7	105,345
1940-41 ..	70,129	80.5	17,010	19.5	72,818
Averages ..		82.2		17.8	

Since Australia produces a large surplus of sulphide concentrates, much of which is wasted and which can be used for the manufacture of sulphuric acid,

the inference to be drawn from the above tables is that most of the sulphur imported can be replaced by using home produced sulphide concentrates.

As the average annual value of the sulphur imported into Australia for seven years before the war was £438,000, it is a business well worth diverting to home industry. The desirability of doing this has long been recognised and has been assisted by the Commonwealth Government by the payment of a bounty on home-produced sulphur since 1923. There are practical difficulties to be overcome in this substitution, but they are not insurmountable. Ultimately the deciding factor is of course the cost of superphosphate. Considerable substitution had occurred before the war and this has continued, the most notable new development being the use of pyrite concentrates from Norseman in substitution for imported sulphur in Western Australia. Since the British evacuation of Nauru and Ocean Island there has been drastic rationing of phosphate rock, and this in turn has meant that less sulphuric acid has been required for the manufacture of chemical fertilisers. The combination of shortages of both sulphur and phosphate rock has thus facilitated the process of substituting sulphide concentrates for sulphur in sulphuric acid plants.

It is interesting to note the movements of sulphides produced in Australia, as shown in the accompanying map (Figure 10). There is a good deal of

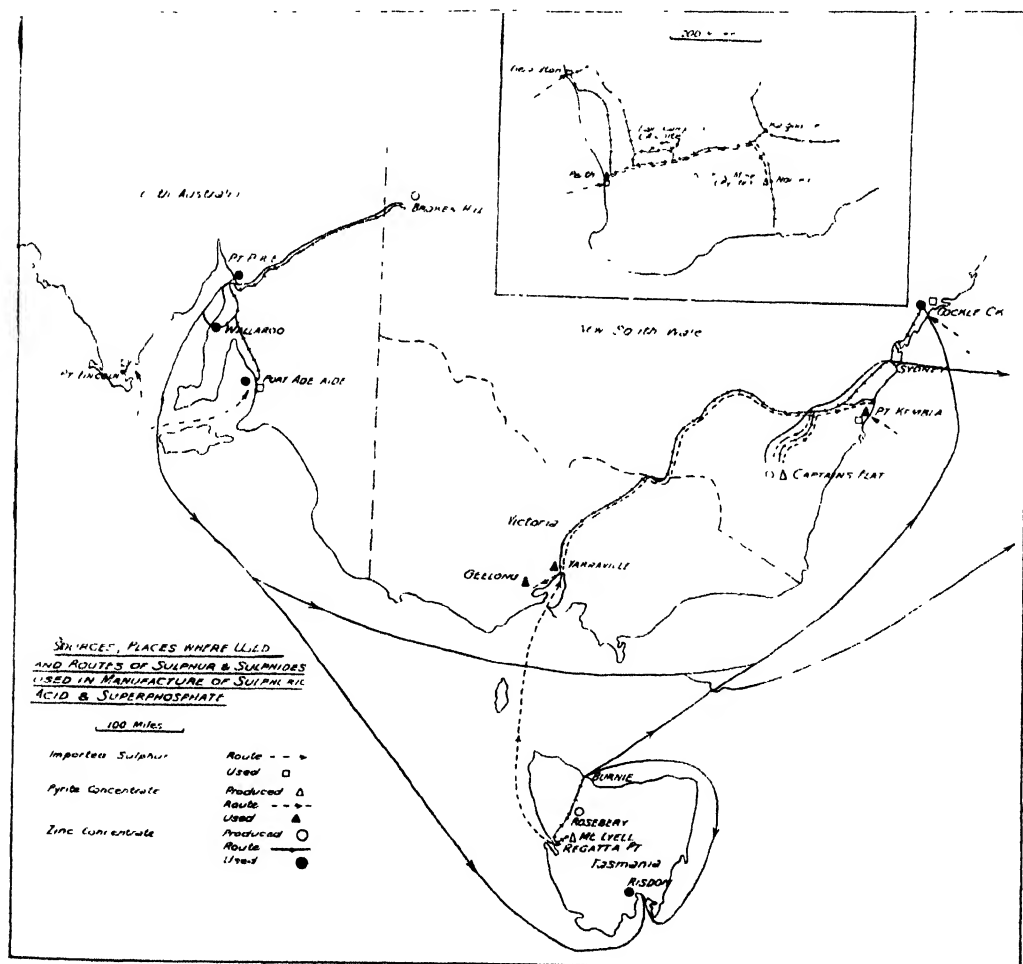


Fig. 10.

unnecessary transport used by this arrangement and the transportation of pyrite concentrates, 50% only of which is sulphur, is also wasteful in itself. The ideal would be to manufacture elemental sulphur from sulphide concentrates in sufficient quantity to satisfy such requirements. Another alternative would be to transport acid, but that is very difficult. Australian producers of sulphides and especially those interested in the manufacture of sulphuric acid, are well aware of the advantages of transporting sulphur as compared with sulphides and it is believed that ultimately elemental sulphur will be produced in Australia in sufficient quantities to satisfy all domestic requirements.

Phosphate Rock. From consideration of sulphur and sulphuric acid we pass naturally to phosphate rock. The Australian farmer has been encouraged to use the highest grade superphosphate fertilisers, and when war began consumption of such fertilisers had reached a high figure. For its phosphate this fertiliser industry depended upon high grade rock from Nauru and Ocean Island, both of which are now in Japanese hands. In the year ended 30th June, 1939, imports from these sources amounted to 800,422 tons, valued at £829,061.

Loss of this phosphate is likely to have serious consequences upon certain phases of our pastoral and agricultural industries; hence the necessity for intensive prospecting and development of our indigenous resources. There seems little prospect of producing much phosphate rock in Australia, suitable for use in the manufacture of superphosphate, but considerable quantities of lower grade rock containing about 40% tricalcic phosphate and 10% ferric oxide and alumina are available in South Australia.

Arrangements for using the small quantities of guano and phosphate rock still available on the Abrolhos Islands, W.A., are well advanced and a thorough investigation is being made of the deposits in the Dandaragan district in W.A. At this locality a reserve of 100,000 tons of rock with 25-35% tricalcic phosphate has been proved. The phosphate occurs as nodules in a zone up to four feet thick under relatively high overburden. Commercial use of this rock is obviously going to be difficult.

Phosphate deposits are being investigated also at Holbourne Island, Queensland, Molong-Canowindra, New South Wales, and Mansfield, Victoria, but the prospect of worthwhile production from them is not viewed very hopefully.

Phosphate rock sufficient for the production of high-phosphorous pig iron is available in South Australia.

NON-METALLICS.

I pass now to a diverse group of minerals—the non-metallics. With a few notable exceptions this large group is apt to escape notice, especially in wartime, when attention is focused on the implements of war and thus on steel, aluminium and the metals generally. Growth in the consumption of the non-metallics is almost as true a guide to the degree of a country's industrial development as its consumption of steel. This is particularly evident of course when we consider the refractories, the use of which increases side by side with steel. Compared with our metal industry our non-metallic industry is only a healthy baby.

Some industries have been founded directly on domestic non-metallics consequent upon the local demand becoming large enough, but development has also come about in other ways. A company engaged chiefly in manufacture abroad may find it expedient to commence a branch factory in Australia. Commonly it does so on the basis of a raw material to which it is accustomed, but after a time it may find that supplies near at hand are quite as suitable as that which it has been importing. The white clay industry is an outstanding example of this. War or industrial trouble by causing a check to, or cessation of, a mineral supply may lead to the local article being tried. As an example

we may take the talc industry which during this war has found Indian talc just as suitable as Italian and is now being forced to go more carefully into examining the possibility of using Australian, in part or wholly.

War demands and restrictions of imports have led to a greatly increased demand on domestic sources of supply of most non-metallic minerals. It is desirable that as much of this trade as possible should be retained after the war. The responsibility for this rests mainly with the producer and the processor (whose attitude to the problem is however governed to some extent by the volume of trade in individual minerals), but Government can and is doing much to establish production of many of these minerals on a sound basis. So far there is so little beneficiation practised that we are virtually trying to replace the carefully prepared article imported before the war with processed raw minerals.

The Australian prospector has not helped himself as much as he might in fostering the use of Australian non-metallic minerals. He is apt not to send bulk parcels true to sample, and that is something industry will not stand. The consumer, for his part, could sometimes be a little more generous as to price. He is apt to ask the prospector at what price he can supply when he very well knows in many cases what he can afford to pay. From this you may conclude I am not a business man. That depends upon your viewpoint.

To attempt a summary of the non-metallic industry of Australia in the course of this address would be quite impossible. It may indeed be doubted whether anyone is yet in a position to do this. There are men in the mining industry in Australia who could tell you all you want to know about silver, lead, zinc, copper; others who could tell you all about tin, and a good deal about tungsten, antimony, bismuth, but I know of no person or company who could tell you all about clay, diatomite, barite, talc, to mention only a few non-metallics. Trade knows no State boundaries, and the number of companies which handle some non-metallics is very large compared with the few which deal with metals.

Some members of this audience will realise that one could deal with minerals as non-metallic in themselves or as ores of metals. In fact I have dealt with beryl as the ore of beryllium rather than as a non-metallic mineral constituent of pegmatites and as such perhaps to be described with feldspar and mica. Magnesite also has been referred to as the principal ore of magnesium, and its use as a refractory passed over.

In looking through the list of non-metallic minerals it will be found that most of them are required for the same purposes in war as in peace. They are not required directly for arms and munitions but have some vital use in industrial production or in the manufacture of some article or articles the need for which is thrown into sharp relief by the war. Perhaps the micas and quartz crystals are outstanding examples.

The *micas* are a well-known group of rock-forming minerals, which in a few places in the world occur in sufficiently large masses to become economically valuable. We are concerned only with the potassium mica, muscovite and the magnesium mica, phlogopite.

Seventy-five per cent. of the world's pre-war production of muscovite came from India and 10% from the U.S.A. Practically all the phlogopite came from Canada and Madagascar, which countries have been in keen competition, with Madagascar leading in recent years.

Muscovite and phlogopite have rather different uses; the former is chiefly now required for spark plug wrappings and radio condensers, the latter chiefly for heat insulating washers on spark plugs, though it is also used as a wrapper in some types of plugs (*vide* Figure 11). It will be realised that the enormously expanded aircraft industry calls for greatly increased quantities of high quality

sheet mica. At the same time the prohibition placed on the manufacture of such articles as radiators, toasters and flat irons increases the cost of producing mica by taking away an outlet for somewhat inferior sheet.

The principal muscovite deposits occur in the Harts Range and along the Plenty River, distant respectively 150 and 200 miles north-easterly from Alice Springs. Other deposits to which attention is being given are those at Morehead River, 100 miles north-west of Laura, Mount Kitchen, 40 miles west of Mungana, and Yinnietharra, on the Gascoyne River 150 miles east of Carnarvon.

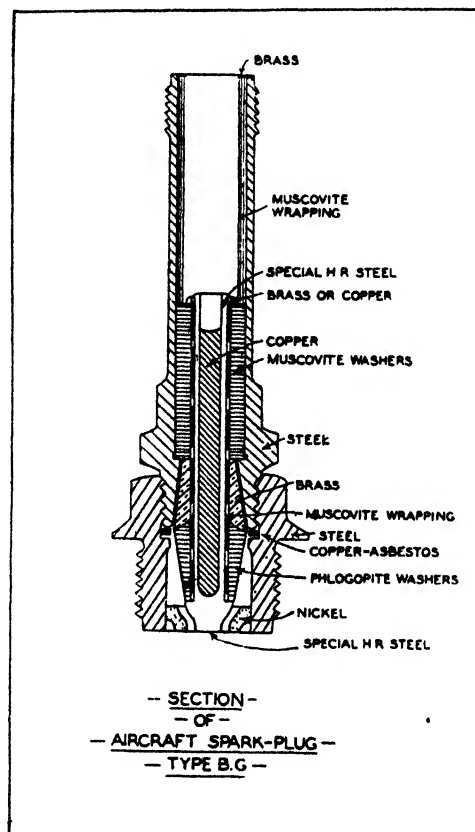


Fig. 11.

Phlogopite is being mined at Strangeways Range, 42 miles east-north-east of Alice Springs. The more important mica localities are shown in Figure 12.

Nature certainly contrived to put all these deposits in out-of-the-way places.

Muscovite has been produced from central Australia since 1890, but mining was only intermittent until 1928. The mining of phlogopite is a wartime development.

A feature of mica pegmatites not generally recognised is their extreme irregularity. This is not invariably so, but it is true of a great number. When in addition it is remembered that the distribution of the mica within the dyke is sporadic and that there is a very large amount of waste it will be realised that high quality mica is a valuable commodity, especially in the larger sizes. Prices ruling in Australia have been fixed by the Prices Commissioner and range from 2s. 3d. per lb. for spotted mica and washer size (not less than $1\frac{1}{2}$ sq. inches) to 60s. per lb. for clear mica of special size (not less than 60 sq. inches).

You have probably all seen the recent newspaper articles on the mica mining activities in the Northern Territory, which are now under the control of the Allied Works Council with the Controller of Minerals Production providing technical advice. The Department of Supply and Shipping is now the sole mica purchasing authority in Australia.

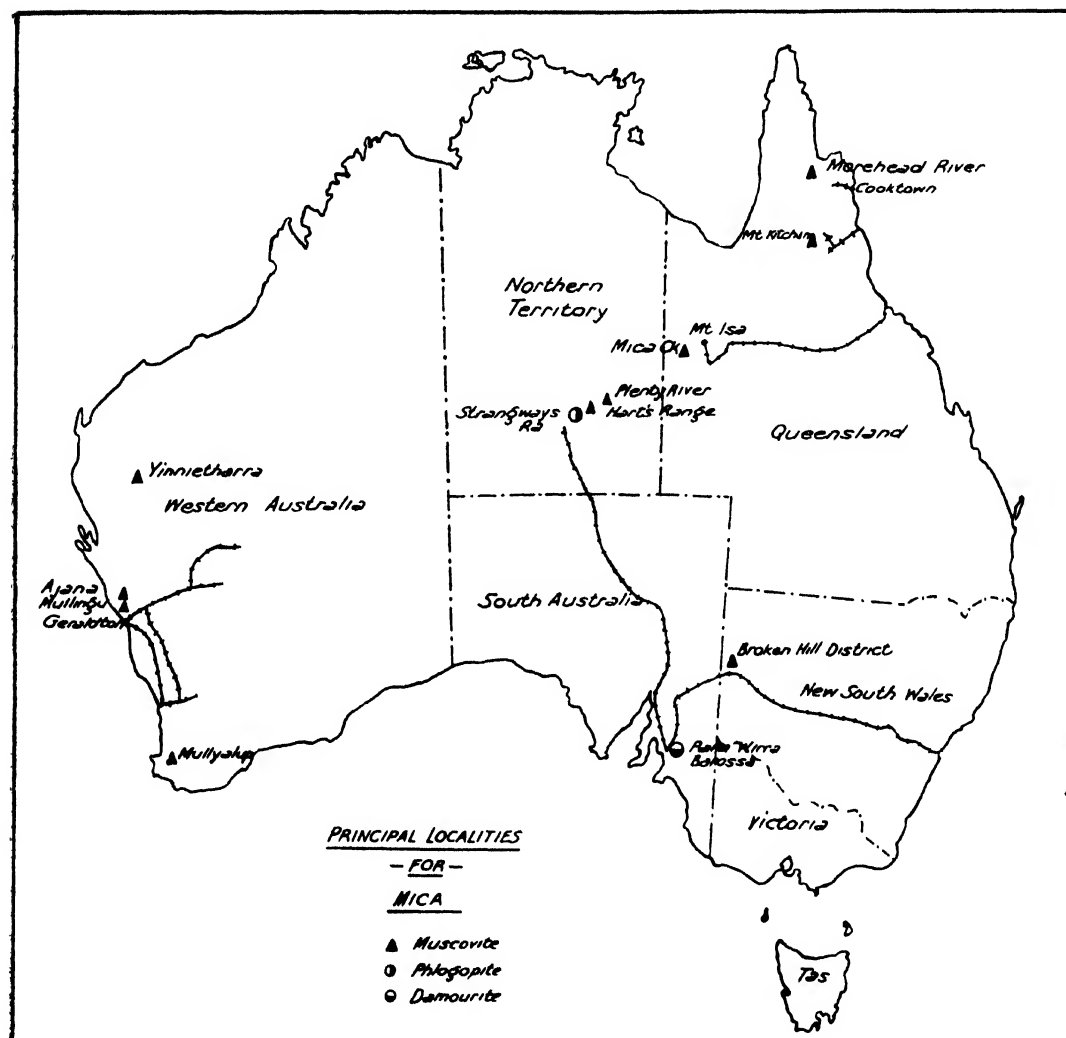


Fig. 12.

Quartz crystals are very much sought after these days. If any of you have crystals on your mantelpieces or in your offices as paper-weights, you should take them along to the Mines Department. They may be useful and valuable.

Crystallised quartz, among a few other substances (e.g. tourmaline), possesses the property of generating an electrical potential when placed under stress. Conversely, if an electric charge is applied to a plate of the material in a certain manner, a change in its dimensions results. This phenomenon, known as the piezo-electric effect, is made use of in a variety of ways; notably in telephony and telegraphy, wireless transmission, ballistics, depth recording, direction finding and radio-location. In all these applications the quartz crystal is

employed as a resonator or oscillator for the accurate frequency control of an electrical circuit operating at radio frequency. The frequency of operation is entirely a function of the thickness of the crystal plate used and its relationship to the crystallographic axes of the original crystal. Highly skilled technicians are needed for the preparation of such crystal plates. (See Figure 13.)

Despite the fact that quartz is an extremely abundant constituent of the earth's crust, flawless, untwinned specimens, suitable for use in resonator circuits, are rare. Prior to the outbreak of war practically the whole of the world's supply was obtained from Brazil and Madagascar.

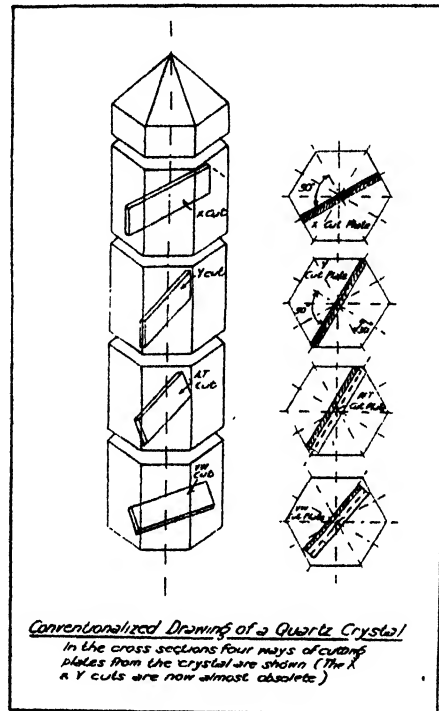


Fig. 13.

As a result of the war there is an unprecedented demand on the part of the Army, Air Force and Navy for equipment which depends entirely on the use of piezo-electric quartz for its proper functioning, and considerable difficulty is now being experienced in maintaining supplies. It may be deduced from the fact that specifications have been made less and less rigid that requirements are not being met satisfactorily. It may now be said that unflawed and untwinned crystals measuring about 1 inch by 1 inch in cross-section normal to the long axis and about 1 inch long can be used, though larger sizes are preferred. Some kinds of twinning are not objectionable in large crystals.

The molybdenite-bearing pipes of the Glen Innes district, New South Wales, offer the best chances of production, but many other prospects are being explored.

The remaining non-metallic minerals I must now pass over in rather rapid review.

Australia's requirements of amorphous and of some kinds of fine-grained flake *graphite* are being met chiefly by production from Collinsville in Queensland and Uley in South Australia, but it is still necessary to import most if not all our requirements of crystalline and of higher grade and coarser grained flake.

The domestic demand for lower grade *barite* and *talc* (including *steatite* and *pyrophyllite*) can be satisfied from sources in South Australia, Western Australia and New South Wales, but there is a great need for supplies of the higher grades of both minerals. If this need can be satisfied there is a good prospect of the trade being held after the war. Figures 14 and 15 show graphically how production of barite and the talc minerals has increased in recent years. These may be taken as typical of most non-metallic minerals.

In the ceramic industry most requirements of *clay* are being filled but there is a strong demand for a good plastic refractory clay. The greatly increased production of *felspar* is coming chiefly from Coolgardie, Broken Hill and Gumeracha.

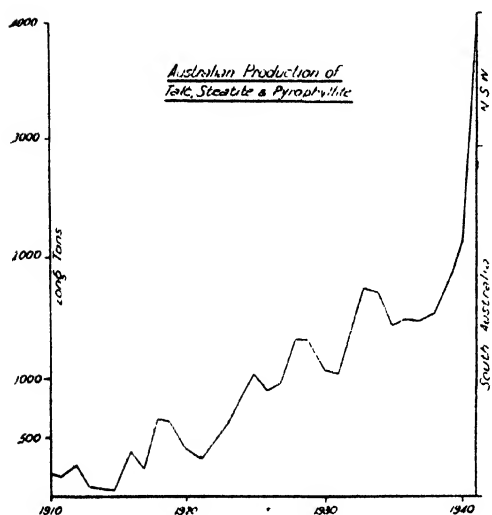


Fig. 14.

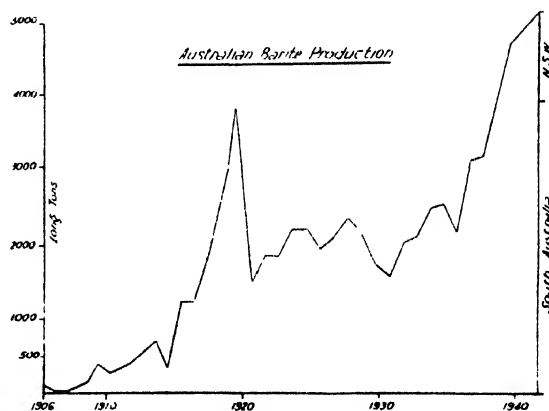


Fig. 15.

Some paint manufacturers (and paint is important in the war effort) are greatly in need of good yellow *ochre*. The fact that supplies of ochre are still being drawn from Rumbalara in the Northern Territory is both a tribute to the quality of that deposit and evidence of the need. Considerable reserves are believed to be available in this locality.

Fluorite is available in sufficient quantities and research is proceeding in the preparation of synthetic cryolite therefrom, which will be required when the manufacture of ingot aluminium commences.

In discussing *asbestos* it is necessary, because of their different uses, to distinguish clearly between the three main kinds which may be referred to as chrysotile, crocidolite (or blue amphibole) and white amphibole asbestos.

There are large reserves of crocidolite in the Hamersley Range, Western Australia, and supplies are coming forward from this source in adequate quantities. There are also ample supplies of white amphibole asbestos, chiefly anthophyllite from Bindi Bind in Western Australia and tremolite from the Lewis Ponds area in New South Wales. The amounts of blue and white amphibole asbestos produced in Australia in 1940 were considerably larger than in any previous year.

Very large importations of chrysotile asbestos however are still necessary. In the year ended June, 1939, these amounted to 9,217 tons, valued at £178,494, and were obtained from Canada, Rhodesia and the Union of South Africa. Local production, though small, shows a rising tendency. A new development is

the formation of a subsidiary company by Colonial Sugar Refining Co. Limited to work chrysotile deposits between Zeehan and Renison Bell, Tasmania.

The aluminium silicates, chiefly *sillimanite* and *kyanite*, are in demand as refractories. Australia is self-sufficient in sillimanite, supplies of which are obtained from Broken Hill, New South Wales, and Mount Crawford, South Australia. Some kyanite deposits in Northern Territory and South Australia have been investigated lately but it seems as though we shall have to continue to rely on imports of this mineral from India unless sillimanite can be wholly substituted therefor. Trial parcels of sillimanite have been sent to the United States and a small export trade may result. Our known reserves are not large enough to permit other than limited export.

Diatomite, or diatomaceous earth, is a most interesting industrial mineral. It has two principal uses: filtration and insulation, and many minor ones including fillers and abrasives. Diatomite, as you know, is composed of the minute frustules of aquatic plants known as diatoms of which there are many different kinds. The assemblage of diatoms present in the diatomite determines its use. Generally if there is a mixture of long, thin, filiform and rounded honeycomb forms present, a diatomite is suitable for filtration, but if the forms present are ovate, cylindrical and boat-shaped it will be far less efficient as a filter medium though suitable for all other purposes. The extensive Californian deposits are the best known of the former type and filter aids based on this diatomite set the world standard. (Pre-war import of Californian filter aids into Australia amounted to approximately 3,000 tons.) In Queensland and New South Wales there are considerable reserves of the latter type in which *Melosira* is the principal form present. The Victorian diatomites are much more suitable than those of other States for filtration uses but, unfortunately, reserves are believed to be small. Something might also be done with the deposits of Recent Age in Western Australia and some interesting material has recently been received from northern Queensland and South Australia but the outlook for large-scale substitution of Australian diatomite for imported Californian for the most exacting filtration requirements is not particularly promising. However, diatomite requirements for all uses other than filtration can be supplied without difficulty from New South Wales and Queensland.

The amount of diatomite consumed in Australian industry is quite considerable, being about 7,000 tons, of which somewhat less than half has been imported. The graph, Figure 16, shows how markedly production of diatomite has increased in the past ten years.

SOME GENERAL CONSIDERATIONS.

There is no doubt that in respect to knowledge concerning her resources of many metals and minerals Australia was caught at a great disadvantage compared with say Canada, India and U.S.A., all of which countries have national geological surveys and two of which have a Bureau of Mines as well. The most sketchy statements had to be compiled concerning these and other metals and minerals, which ought to have been ready before the war commenced. Take one example. It has happened that a demand has come for a mineral (beryl for instance), most of which could be met from one mine in one State. Before this could be found out, every State in the Commonwealth had to be written to and the replies examined comparatively. The essentials of this information ought to have been available in advance. I know I run the risk of being suspected of being a propagandist for my own ends, but I am prepared to run that risk because I am so certain that what I have said is true. And what is true in war should be true in peace-time. Demands usually do not arise so sharply in peace-time and the need may be less obvious, but they are there nevertheless.

In this war calls have been made upon Australia by the allied nations for production of certain minerals and metals. In some instances long delay has been caused because insufficient information was available upon which to base an answer or plan a production programme. Recently the outline of a plan to establish a United Nations Relief and Rehabilitation Administration has been released by the Australian Prime Minister. This plan clearly visualises pooling and sharing of resources along much the same lines as is being followed during the war. If the organisation there proposed comes into being it will be absolutely essential that information concerning all Australia's resources shall be available through unified channels.

Part of the job of the Branch which I direct has been, in conjunction with the Controller of Minerals Production and Minerals Committee, and of course the State Mines Departments, to make a survey of certain of Australia's mineral resources. This work is full of absorbing interest and the most aggravating

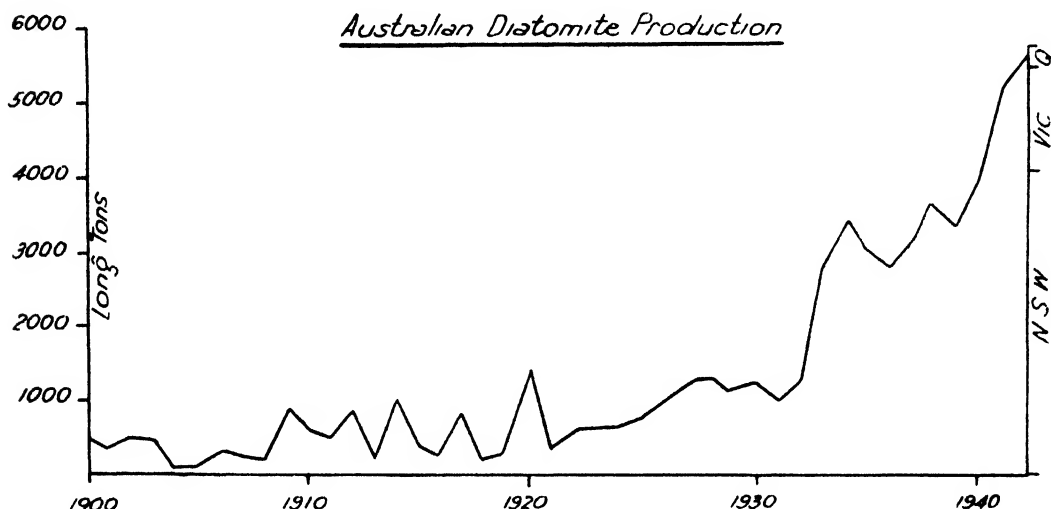


Fig. 16.

complexities. The Mines Departments of the States have a very good knowledge of mineral resources within their own borders, but something more than that is required for the planning of Australian industry. We want to know as much as possible about our mineral deposits on an Australian as well as a State basis. We also want to know what happens to the products of the mining industry. Until recently this has been nobody's business. Take a common commodity such as clay. A clay produced in New South Wales is sold to an agent in Victoria. So far as New South Wales is concerned that is the end of the story; Victoria isn't interested and in fact is probably unaware of the transaction. By tracing what happened to the clay we find half of the production was used to make telephone insulators in Victoria and the other half found its way into a paper mill in Tasmania. Knowing that the clay is used for such purposes we are able to advise likely consumers. This is one way in which the Commonwealth supplements the work of the States and assists the development of their mineral industries.

Another most important aspect of mining in the present war may be conveniently stressed here and that is—manpower. In the war of 1914–1918 there was nothing like the call upon Australian manpower as in this. Hundreds of prospectors, gougers and small scale miners were left free to pursue their activities and under the stimulus of high prices these men contributed valuable

quantities of ores of tin, tungsten, molybdenum, copper and other metals. This condition not only does not pertain today, but the mining industry has had to compete with others for men, machinery, transport and all essential supplies. These remarks are not made in a spirit of criticism but merely to state the facts. The effect of all this is that almost every operation—even a very small one—has to be planned and government is inevitably involved, if not in the actual mining, then in the supply of some essential requirement.

Having regard to her small population, Australia is making a noteworthy contribution to the united nations' need for mineral supplies. Mining is a hazardous business at any time and it is inevitable that in the hasty planning which has been demanded some mistakes will have occurred and money spent for little return. Critical attention is apt to be focused on such expenditure, and the favourable side of the story overlooked. An immense amount of information concerning our mineral resources has been gathered during the war which will be of permanent value; a stimulus has been given to some kinds of production which should develop into a permanent feature of Australian industry; in some directions we have a definite picture where before we had merely hazy notions; and some noteworthy discoveries have been made, outstanding among which is the size and value of the King Island scheelite deposit.

It is a pleasure to record the assistance given in preparing this address by my colleagues in the Department of Supply and Shipping and to all those in the mining industry who have so freely made information available.

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SIMPLE REGRESSION AND CORRELATION.

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This paper, which is partly expository, has been prepared with a view to making the mathematical theory of statistical regression and correlation more accessible to students. An attempt is made to clarify some important points in the theory of polynomial regression, and a simple proof of the distribution of the coefficient of normal correlation is appended. The only published proofs of this distribution known to the author either require the notions of n -dimensional geometry or introduce heavy and involved multiple integration (Fisher, 1915; Uspensky, 1937; Plummer, 1940).*

Many references are made herein to an earlier paper by the present writer which showed that the χ^2 , "Student's" t , Fisher's z , and Cauchy distributions are most easily described for practical statistical purposes in terms of Gamma and Beta functions in their simplest forms as used by Bayes and other skilful 18th century mathematicians. That paper is quoted briefly as "E.P."*

I. ESTIMATES OF COEFFICIENTS OF REGRESSION FROM SAMPLES.

The theory of statistical covariation or "correlation" has been closely studied for a class of cases in which the mean value of one variate Y among those members of a collection of objects O which have any particular value of another variate X is a simple polynomial in X , that is

$$M_x(Y) = c_0 + c_1X + c_2X^2 + \dots$$

to a limited number of terms. This equation of mean values of Y is for historical reasons called the equation of "regression" of Y on X .

Putting $X = M(X) + x$, we have the alternative form

$$M_x(Y) = b_0 + b_1x + b_2x^2 + \dots$$

When all the members of the bivariate collection are known and b_0, b_1, b_2, \dots are true coefficients of regression, we have the identities

$$\left. \begin{aligned} M(Y) &= b_0 + b_2\mu_2 + \dots \\ M(xY) &= b_1\mu_2 + b_2\mu_3 + \dots \\ M(x^2Y) &= b_0\mu_2 + b_1\mu_3 + b_2\mu_4 + \dots \end{aligned} \right\} \dots\dots\dots (1)$$

and so on indefinitely

where the mean values now refer to the whole collection.

These moment equations express the coefficients b_0, b_1, b_2, \dots in terms of the product moments of Y with successive powers of x , and the moments of X about the mean $M(X)$. But in practice we have only a sample, large or small, of the members. The natural procedure then is to operate on the sample in the same way as we would on the whole of the members if they all were given. We shall thus derive estimates of the true coefficients of regression.

Although there is no guarantee that an estimate of a coefficient derived from a sample of 40 members will be actually nearer to the true value than one

* See references at end of paper.

derived from 20 members, it will be exemplified presently in simple cases that among estimates from 40 members there is a smaller dispersion than among those derived from 20 members, and generally, that the standard error of an estimate tends to vary inversely as the square root of the number of members on which it is based, and so to follow the general statistical rule.

In many practical cases of "regression", such as the progression of the length of a metal tape on increasing temperature, or of the calorific intake of children on increasing age, both the theory and the computations are much simplified by selecting a sample so that the values of the under-variate are symmetrically distributed, although this may be inconsistent with its actual distribution. Thus if the ages of the children under investigation are 7, 8, . . . 13 years last birthday, we may take the same number of age 13 as of age 7, the same number of age 12 as of age 8, and so on.

Supposing first that the equation of regression of Y on X is linear, namely $M_x(Y) = b_0 + b_1x$, and that the values of X are symmetrically distributed, we have from equations (1)

$$M(Y) = b_0$$

$$M(xY) = b_1\mu_2$$

$$M(x^2Y) = b_0\mu_2$$

$$M(x^3Y) = b_1\mu_4$$

and so on indefinitely.

When all the members are known, all these equations are satisfied by the true values of b_0 and b_1 . But with only a sample of the members available (in which X is still assumed to be symmetrically distributed), we have a choice of various estimates of b_0 , namely $M(Y)$, $M(x^2Y)/\mu_2$, $M(x^4Y)/\mu_4$, . . . and of b_1 , $M(xY)/\mu_2$, $M(x^3Y)/\mu_4$, $M(x^5Y)/\mu_6$, . . . where all the quantities now refer to the sample. If the variance of Y about its mean value is the same for all values of X , and therefore of x , we may easily compare the variances of these alternative estimates of b_0 and of b_1 , by supposing the values of X fixed and only the values of Y variable. Taking $M(x^2Y)/\mu_2$ for example, this is a linear function of $Y_1, Y_2, \dots Y_n$, there being n members in the sample, and writing it as

$\frac{1}{n\mu_2} \sum_{i=1}^n x_i^2 Y_i$ its variance is seen to be $\frac{S(x^4)}{n^2\mu_2^2} s^2$ or $\frac{\mu_4}{n\mu_2^2} s^2$, where s^2 is the common variance of the distributions of $Y_1, Y_2, \dots Y_n$. Thus the above estimates

of b_0 have successively the variances $\frac{1}{n} s^2, \frac{\mu_4}{n\mu_2^2} s^2, \frac{\mu_8}{n\mu_4^2} s^2, \frac{\mu_{12}}{n\mu_6^2} s^2, \dots$. Similarly

for b_1 we must consider the series of multipliers $\frac{\mu_2}{n\mu_2^2}, \frac{\mu_6}{n\mu_4^2}, \frac{\mu_{10}}{n\mu_6^2}, \frac{\mu_{14}}{n\mu_8^2}, \dots$

That each of these two series is divergent may be shown by Cauchy's inequality (Hardy, Littlewood and Polya, 1931). For example, in the case of the second series we have the inequalities (i) $\mu_4^2 < \mu_2\mu_6$, (ii) $\mu_6^2 < \mu_4\mu_8$, (iii) $\mu_8^2 < \mu_6\mu_{10}$, (iv) $\mu_{10}^2 < \mu_8\mu_{12}$. . . and (i) shows that the 1st term of the series is less than the 2nd; the square of (ii) multiplied by (iii) shows 2nd < 3rd; (iii) by (iv) shows 3rd < 4th, and so on. Hence it appears that the estimates of b_0 and b_1 which show the least dispersion are those calculated from $M(Y)$ and $M(xY)/M(x^2)$ respectively.

It may be shown similarly (although the inequalities are more complicated) that for polynomial regression of higher degree the estimates of the coefficients which show the least variance are those which are derived from the moment equations of lowest possible degrees. As these are the equations which appear when the coefficients are chosen by minimizing the sum of squares of deviations of the sample values of Y from their corresponding mean values as derived from

the regression equation, we thus have some practical justification for applying the "method of least squares" to this particular problem.

If, further, it can be assumed that the distributions of Y for the various values of X are all normal (as well as having the same variance), and if the degree of the regression equation is known, the distributions of the estimates of the coefficients of regression for fixed sample values of X may be determined.

For example, when the regression equation is quadratic for the specified values of X (supposed symmetrically distributed), it may be written conveniently in the form

$$M_x(Y) = \beta_0 + \beta_1 x + \beta_2 (x^2 - \mu_2),$$

where $\beta_0, \beta_1, \beta_2$ are true coefficients and $x = X - M(X)$.

Applying the moment equations of lowest degree to the sample of n members, we find estimates b_0, b_1, b_2 from the equations

$$\left. \begin{aligned} M(Y) &= b_0 \\ M(XY) &= b_1 \mu_2 \\ M\{(x^2 - \mu_2)Y\} &= b_2 M\{(x^2 - \mu_2)^2\} = b_2 (\mu_4 - \mu_2^2) \end{aligned} \right\} \dots \dots \dots (2)$$

Denoting by s^2 the common variance of the normal distributions of Y for the various values of X , we have the n statistically independent standard normal variates $\eta_r (r = 1 \dots n)$

where $\eta_r = \{Y_r - M_x(Y)\}/s = \{Y_r - \beta_0 - \beta_1 x_r - \beta_2 (x_r^2 - \mu_2)\}/s$.

Forming a set (ξ) orthogonal to the set (η) , such that (E.P., p. 214)

$$\xi_1 = \frac{1}{\sqrt{n}} (\eta_1 + \eta_2 + \dots + \eta_n) = \frac{1}{\sqrt{n}} \frac{n(b_0 - \beta_0)}{s} = \frac{\sqrt{n}(b_0 - \beta_0)}{s},$$

$$\xi_2 = \frac{1}{\sqrt{S(x^2)}} \sum_1^n (x_r \eta_r) = \frac{1}{\sqrt{n\mu_2}} \frac{n(b_1 - \beta_1)\mu_2}{s} = \sqrt{n\mu_2} \frac{b_1 - \beta_1}{s},$$

$$\xi_3 = \frac{1}{\sqrt{S\{(x^2 - \mu_2)^2\}}} \sum_1^n \{(x^2 - \mu_2) \eta_r\} = \sqrt{\{n(\mu_4 - \mu_2^2)\}} \frac{b_2 - \beta_2}{s},$$

we have $\sum_1^n S(\xi^2) = S(\eta^2)$, and $\sum_1^n S(\eta^2) - (\xi_1^2 + \xi_2^2 + \xi_3^2)$ is a χ^2_{n-3} .

Writing $s\eta_r$ in the form

$$Y_r - b_0 - b_1 x_r - b_2 (x_r^2 - \mu_2) + (b_0 - \beta_0) + (b_1 - \beta_1)x_r + (b_2 - \beta_2)(x_r^2 - \mu_2),$$

it appears that

$$s^2 \sum_1^n S(\eta^2) = \sum_1^n \{Y_r - b_0 - b_1 x_r - b_2 (x_r^2 - \mu_2)\}^2 + n(b_0 - \beta_0)^2 + n\mu_2(b_1 - \beta_1)^2 + n(\mu_4 - \mu_2^2)(b_2 - \beta_2)^2,$$

as the product terms vanish because of the three moment equations.

Hence $S\{Y - b_0 - b_1 x - b_2 (x^2 - \mu_2)\}^2 / s^2$, which we may denote by $S(r^2) / s^2$, is a χ^2_{n-3} and the three fractions

$$\frac{\frac{\sqrt{n}}{\sqrt{\{ \frac{1}{n-3} S(r^2) \}}} \cdot \frac{(b_0 - \beta_0)}{s}, \quad \frac{\sqrt{n\mu_2}}{\sqrt{\{ \frac{1}{n-3} S(r^2) \}}} \cdot \frac{(b_1 - \beta_1)}{s}, \quad \frac{\sqrt{\{n(\mu_4 - \mu_2^2)\}}}{\sqrt{\{ \frac{1}{n-3} S(r^2) \}}} \cdot \frac{(b_2 - \beta_2)}{s} \dots \dots \dots (3)$$

are t_{n-3} variates (E.P., p. 223).

When the sample is of a useful size, say 30 or more members (or values of Y), the t distribution is nearly normal and then b_0, b_1, b_2 may be regarded as distributed nearly normally about their true values with standard deviations

$$\sqrt{\left\{ \frac{1}{n-3} S(r^2) \right\}} / \sqrt{n}, \quad \sqrt{\left\{ \frac{1}{n-3} S(r^2) \right\}} / \sqrt{n\mu_2}, \quad \sqrt{\left\{ \frac{1}{n-3} S(r^2) \right\}} / \sqrt{\{n(\mu_4 - \mu_2^2)\}} \dots \dots \dots (4)$$

where $S(r^2)$ is the sum of squares of the residual deviations, that is the deviations of the n observed values of Y from the corresponding mean values of Y as calculated from the regression equation with the estimated coefficients b_0, b_1, b_2 .

The denominators of expressions (4) of course appear immediately when the moment equations (2), which are linear in the variable values of Y , are used to express the standard deviations of b_0, b_1, b_2 , in terms of the common standard deviation of the distributions of Y for the various values of X ; while the numerator $\sqrt{\left\{\frac{1}{n-3}S(r^2)\right\}}$ is the well known estimate of this common standard deviation allowing for the fact that the n residual deviations of Y , being connected by three moment equations in this case, supply only the same amount of information regarding the standard deviation as $(n-3)$ statistically independent residuals would. The virtue of the foregoing algebraical analysis (initiated for b_0 and b_1 by R. A. Fisher, 1926) is that it shows that, under the postulate of normal distribution of Y with common variance for each value of X , the estimates b_0, b_1, b_2 , are statistically independent of one another and of the sum of squares of residuals, and therefore that each b is expressible in terms of a t variate. (Fisher and Yates (1938) also consider all the coefficients in the case of one value of Y at each of a series of equispaced values of X .)

Similarly if the regression equation is of the 3rd degree and is written in the form

$$M_x(Y) = \beta_0 + \beta_1 x + \beta_2 (x^2 - \mu_2) + \beta_3 f_3(x)$$

where $f_3(x)$ is of the 3rd degree and such that $M\{f_3(x)\} = 0$,

$$M\{xf_3(x)\} = 0, \quad M\{(x^2 - \mu_2)f_3(x)\} = 0,$$

X being symmetrically distributed in the sample, we calculate b_3 as an estimate of β_3 from the sample value of $M\{f_3(x) \cdot Y\} / M\{[f_3(x)]^2\}$. Putting $f_3(x) = x^3 + ax$, the above mean value conditions give $a = -\mu_4/\mu_2$, and we derive

$$b_3 = M\left\{ \left(x^3 - \frac{\mu_4}{\mu_2} x \right) Y \right\} / (\mu_6 - \mu_4^2/\mu_2),$$

and a further standard normal variate

$$\sqrt{\{n(\mu_6\mu_2 - \mu_4^2)/\mu_2\}} \cdot \frac{b_3 - \beta_3}{s} \dots \dots \dots (5)$$

There are now four t_{n-4} variates with the new denominator $\sqrt{\left\{\frac{1}{n-4}S(r^2)\right\}}$

instead of that in expressions (3), where $S(r^2)$ now denotes the sum of squares of residual deviations from the altered regression line, and its divisor indicates that the residuals are now connected by four moment equations.

For regression equations of higher degree the additional "orthogonal" polynomials required become progressively more complicated (Fisher, 1932). It is clear that in equations (1), if X is symmetrically distributed, the odd moments vanish and coefficients of odd powers of x are related exclusively to one set of moment equations and those of even powers including x^0 exclusively to another set. So for $f_4(x)$ we take the form $x^4 + ax^2 + b$ and determine a and b by the mean value conditions for orthogonality; for $f_5(x)$ we take the form $x^5 + ax^3 + bx$ and determine a and b likewise, and so on. One advantage of this method of splitting up a regression equation of uncertain degree into separate orthogonal terms is that the coefficient of each additional orthogonal term and its variance are calculated without affecting the calculations relating to preceding terms. Of course the 3rd orthogonal term not only introduces a coefficient for x^3 but also alters the constant term, the 4th term introduces a

coefficient for x^3 and also alters the coefficient of x , and so on; but when all coefficients of various powers of x are collected, we have the same regression equation as would be derived by using a single polynomial.

It will be clear from the method of deriving (5) that, if b_k is the coefficient of $f_k(x)$, the highest orthogonal polynomial used, we derive the standard normal variate $\sqrt{(nM[\{f_k(x)\}^2]) \frac{b_k - \beta_k}{s}}$, and that the denominator of the t variates is then $\sqrt{\left\{ \frac{1}{n-k-1} S(r^2) \right\}}$.

It follows from expressions (4) that when the sample is fairly numerous the standard errors of the estimated coefficients b vary inversely as the square root of the number of members. Further, if the equation of means is known to be linear, $\frac{1}{2}n$ members at each of two values of X as far apart as possible will give the largest value of μ_2 and therefore the smallest value of the standard error of b_1 ; if the regression equation is known to be quadratic, $\frac{1}{3}n$ members at each of three equispaced values of X as far apart as possible will give the largest values of both $\mu_4 - \mu_2^2$ and μ_2 and therefore the smallest standard errors of both b_1 and b_2 , and, generally, equispaced equifrequent values of X form the best arrangement for keeping the standard errors small.

When the form of the regression equation is unknown, as it usually is in practice, it is obviously desirable to have a substantial number of values Y for each of a considerable number of values of X covering the whole range of interest. It is then possible by graphing the mean values of Y for the various values of X to get an idea of the form of the line of mean values, that is to say of the "line of regression", and also to see, by applying tests for normality and tests for consistency of variance, whether there is reasonable justification for the usual postulate that for each value of X the values of Y are distributed normally with common standard deviation. The graph may suggest, for example, that the line of regression is of periodic, or of logarithmic, or of logistic type, and comparison of the standard deviations may indicate—as it often does in agricultural and biometric data—that the ratio of the standard deviation of Y to its mean value, that is the "coefficient of variation", rather than the standard deviation itself, is the same for the various values of X .

When there is only one member, that is only one value of the variate Y , for each value of X , the fitting of a polynomial can hardly be expected to yield reliable conclusions if there is no prior knowledge of the scale of variation about their hypothetical mean values to which these values of Y are subject. Assuming that the unknown scale is the same for all values of X , an estimate of this "variance" is $S(r^2)/(N-p)$, where N is the number of members of the sample, p the number of coefficients in the regression equation at any stage of the fitting, and $S(r^2)$ the sum of squares of residuals at this stage. Supposing the values of X equispaced, and therefore in this case symmetrically distributed, and denoting the orthogonal polynomials used above by $\varphi_1, \varphi_2, \dots$, we have, using the moment equations,

$$\begin{aligned} S(r^2) &= S\{(Y - b_0 - b_1\varphi_1 - b_2\varphi_2 - \dots)^2\} \\ &= S(Y^2) - Nb_0^2 - S(\varphi_1^2) \cdot b_1^2 - S(\varphi_2^2) \cdot b_2^2 - \dots \end{aligned} \quad (6)$$

So each rise in the degree of the regression equation means a further fall in the sum of squares of residuals. When this equation reaches the $(N-1)$ th degree (involving N coefficients), the moment equations of lowest degree produce a regression equation which is satisfied exactly by each of the N values of Y . Then $S(r^2) = 0$, and $S(r^2)/(N-p)$ takes the indeterminate form $0/0$. Unless there is some knowledge (possibly from a parallel experiment) of the assumed common variance of the variates Y about their mean values, there is no means

of gauging when $S(r^2)$ has reached a reasonable or an "optimum" value and so of judging when to stop the process of introducing further coefficients. We may of course, on the additional assumption of normal distribution of each Y variate, use the t variates (3) to test whether successive coefficients do or do not differ significantly from zero, but the answer to these tests at any stage, whether yes or no, apart from giving no information about higher coefficients, gives no information regarding the significance of $S(r^2)$ at this stage. We might try to meet this difficulty by choosing to stop the regression equation when, after the use of the p th coefficient, $S(r^2)$ first falls below $kS\{(Y - \bar{Y})^2\}$ where k is some fraction such as 0.2 or 0.1 or 0.05; but as $S(r^2)/(N-p)$ is now our estimate of the common variance of the Y distributions, this procedure implies that we regard this latest estimate as being as small as or smaller than it should be, or, perhaps, as not worth further consideration, when it first falls below $k \frac{N-1}{N-p} s_1^2$, where s_1^2 is the corresponding estimate of the variance on the basis of no regression. Failing prior knowledge of the variance this, to say the least, would be an arbitrary rule, although in effect it is often applied. A more logical procedure would be to test at each stage whether the N residuals could fairly be regarded as members of some normal distribution (noting that they are bound by p relations. E.P., 230-238).

On the other hand, if there are at least two values of Y for each value of X , there is available an estimate of the postulated common variance of the Y distributions which is quite independent of the degree of the regression equation. Let X_1, X_2, \dots, X_n be the successive values of X , f_1, f_2, \dots, f_n the corresponding numbers of values of Y , and $S(f) = N$. If the experiment can be designed with the values of X equispaced and $f_1 = f_2 = \dots = f_n$, or at least $f_1 = f_n, f_2 = f_{n-1}$, and so on, so that X is symmetrically distributed and the orthogonal polynomials may be used, the progressive testing of $S(r^2)$ as the degree of the regression equation is raised is made much easier. But in any case, if the estimated $M_x(Y)$ is $b_0 + b_1x + b_2x^2 + \dots$ whether calculated from a single polynomial or a series of orthogonal polynomials, the sum of squares of residuals of the observed values of Y from their respective estimated means is $S\{(Y - b_0 - b_1x - \dots)^2\}$, and when the regression equation is of the $(p-1)$ th degree, the estimated coefficients b_0, b_1, \dots are derived from p moment equations, each linear in the values of Y . So the N residuals are connected by these p linear relations. Assuming that the Y distributions are all normal with common variance s^2 , it can be shown that because of these connections $S\{(Y - b_0 - b_1x - \dots)^2\}$ is the sum of squares of $(N-p)$ normal variates with mean zero and variance s^2 . This proposition has been exemplified in deriving (3) for the case when orthogonal polynomials can be used, and the p normal variates were then separated from the rest.

Performing the summation $S(r^2)$ first for individual values of x and then for all values of x , we have

$$\begin{aligned} SS\{(Y - b_0 - b_1x - \dots)^2\} &= SS\{(Y_x - \bar{Y}_x + \bar{Y}_x - b_0 - b_1x - \dots)^2\} \\ &= SS\{(Y_x - \bar{Y}_x)^2\} + S\{f(\bar{Y}_x - b_0 - b_1x - \dots)^2\} \dots \dots \dots (7) \end{aligned}$$

where \bar{Y}_x is the observed mean. As there are n different values of X the first term on the right side is the sum of squares of $(f_1 - 1 + f_2 - 1 + \dots)$ or $(N-n)$ normal variates with mean zero and variance s^2 . Hence the second term is the sum of squares of $(N-p - N + n)$ or $(n-p)$ normal variates with mean zero and variance s^2 , and all these are statistically independent.

Hence $\frac{S\{f(\bar{Y}_x - b_0 - b_1x - \dots)^2\}}{SS\{(Y - b_0 - b_1x - \dots)^2\}}$ is a Beta variate $b\left(\frac{n-p}{2}, \frac{N-n}{2}\right)$. When

$N-n$ is fairly large (as it should be if reliable results are demanded),

$$S\{f(\bar{Y}_x - b_0 - b_1x - \dots)^2\} \bigg/ \left[\frac{1}{N-n} SS\{(Y_x - \bar{Y}_x)^2\} \right]$$

is a χ^2_{n-p} with sufficient approximation (8)

The computation naturally falls into two parts: first, $S(Y_x)$ for each value of x and $SS\{(Y_x - \bar{Y}_x)^2\}$ are computed from the data; then the moment equations are computed with f values \bar{Y}_x at the corresponding value x , which, of course, produces the same moment equations as those derived by using the individual values of Y .

By using the Beta variate or, when $N-n$ is large, the χ^2_{n-p} variate, we may then calculate the significance of the sum of weighted squares of residuals of observed means from their values as derived from the computed regression equation at any stage, in comparison with the common variance of the distributions as independently estimated from the deviations of the values of Y from their respective observed mean values.

For example, in the case given in R. A. Fisher's "Statistics for Research Workers", Sec. 44, Table 50, we have $N=823$, $n=9$, $p=2$ as linear regression is being tested; $SS\{(Y_x - \bar{Y}_x)^2\}=3,832$, $N-n=814$; $S\{f(\bar{Y}_x - b_0 - b_1x)^2\}=396$, $n-p=7$. Hence $\chi^2_7 = 396 / \frac{3832}{814} > 80$. This value is far beyond the 0.001 significance level, which is reached at about the value 24. So linear regression is not a satisfactory hypothesis and the inclusion in the regression equation of a term or terms of higher degree is indicated.

While the values of X are equispaced in Fisher's example, opposite values of X have unequal frequencies (or numbers of values of Y), so the orthogonal polynomial of 2nd degree cannot be used to test whether quadratic regression would fit the data.

The following example, in which X is symmetrically distributed, illustrates the procedure with orthogonal polynomials.

x	-4	-3	-2	-1	0	1	2	3	4
f	5	5	5	5	5	5	5	5	5
Y_x	$\left\{ \begin{array}{ccccccccc} 2.0 & 2.0 & 3.2 & 5.9 & 4.3 & 5.4 & 6.5 & 5.7 & 6.3 \\ 0.2 & 3.2 & 3.1 & 6.2 & 4.1 & 5.8 & 4.9 & 6.3 & 4.2 \\ 2.9 & 3.8 & 3.4 & 4.2 & 4.2 & 5.9 & 5.9 & 5.8 & 5.3 \\ 1.7 & 2.9 & 2.0 & 4.8 & 4.5 & 5.0 & 5.9 & 7.1 & 5.1 \\ 1.3 & 3.0 & 3.7 & 3.4 & 5.9 & 4.4 & 4.8 & 5.1 & 6.6 \end{array} \right.$								
$S(Y_x)$	8.1	14.9	15.4	24.5	23.0	26.5	28.0	30.0	27.5
$S(xY_x)$	-32.4	-44.7	-30.8	-24.5		+26.5	56.0	90.0	110.0
x^2	16	9	4	1		1	4	9	16
$S(x^2Y_x)$	129.6	134.1	61.6	24.5		26.5	112.0	270.0	440.0
x^4	256	81	16	1		1	16	81	256

$$S(Y) = 197.9$$

$$S(xY) = 150.1$$

$$S(fx^2) = 300, \quad \mu_2 = \frac{300}{45}$$

$$S(x^2Y) = 1198.3$$

$$S(fx^4) = 3540, \quad \mu_4 = \frac{3540}{45}$$

$$\begin{aligned}\text{Hence } b_0 &= \frac{S(Y)}{N} = \frac{197.9}{45} = 4.40, \quad b_1 = \frac{S(xY)}{N\mu_2} = \frac{150.1}{300} = 0.50 \\ b_2 &= \frac{S(x^2Y) - \mu_2 S(Y)}{N(\mu_4 - \mu_2^2)} = \frac{1198.3 - 6.667 \times 197.9}{3540 - 300 \times 6.667} \\ &= -\frac{121}{1540} = -0.08.\end{aligned}$$

When orthogonal polynomials are used, as in this case

$$\begin{aligned}& S[f\{\bar{Y}_x - b_0 - b_1x - b_2(x^2 - \mu_2) - \dots\}^2] \\ &= S(f\bar{Y}_x^2) - Nb_0^2 - N\mu_2 b_1^2 - N(\mu_4 - \mu_2^2)b_2^2 - \dots\end{aligned}$$

Computing $S\left[\frac{1}{f}\{S(Y_x)\}^2\right]$ from the data, this becomes $959.3 - 870.8 - 75.0 - 9.6$.

As $S\{(Y_x - \bar{Y}_x)^2\} = S(Y_x^2) - f\bar{Y}_x^2$ we compute $SS(Y_x^2) = 981.8$.

$$\begin{aligned}\text{Hence } SS\{(Y_x - \bar{Y}_x)^2\} &= 981.8 - 959.3 = 22.5 \\ N - n &= 45 - 9 = 36\end{aligned}$$

$$\frac{1}{N-n} SS\{(Y_x - \bar{Y}_x)^2\} = 0.625.$$

On the hypothesis of linear regression, the sum of weighted squares of residuals of observed means is 13.5 and we have approximately $\chi^2 = \frac{13.5}{0.625} = 21.6$.

This is a very uncommon kind of value, for the total frequency of values of χ^2 not more frequent than this value is of the order of 0.01 . So linear regression is not a satisfactory hypothesis. Trying quadratic regression, the sum of weighted squares of residuals is reduced to 3.9 . To test this approximately we have $\chi^2 = \frac{3.9}{0.625} = 6.2$. This is quite an ordinary value of χ^2 , so we may stop at quadratic regression. The estimated regression equation is

$$\begin{aligned}M_x(Y) &= 4.4 + 0.5x - 0.08(x^2 - 6.67) \\ &= 3.87 + 0.5x - 0.08x^2 \dots\dots\dots(9)\end{aligned}$$

Lastly we note that, using expressions (3) after fitting quadratic regression, the standard errors of b_0, b_1, b_2 , are found by dividing $\sqrt{\left\{\frac{1}{N-3} S(r^2)\right\}}$, where from

$$\begin{aligned}(7) \quad S(r^2) &= SS\{(Y_x - \bar{Y}_x)^2\} + S\{f(\bar{Y}_x - b_0 - b_1x - \dots)^2\} \\ &= 22.5 + 3.9,\end{aligned}$$

by the respective denominators \sqrt{N} , $\sqrt{N\mu_2}$, $\sqrt{N(\mu_4 - \mu_2^2)}$, or $\sqrt{45}$, $\sqrt{300}$, $\sqrt{1540}$. The results are roundly 0.1 , 0.05 , 0.02 . The standard error of the constant term in (9), viz. 3.87 , then is $\sqrt{(0.1)^2 + (6.67 \times 0.02)^2}$ or 0.17 nearly.

II. ESTIMATES OF NORMAL CORRELATION FROM SAMPLES.

Normal correlation is a particular case of linear regression. (Rietz, 1927.)

When two normal variates X, Y with means $M(X), M(Y)$ denoted by A, B and standard deviations $\sqrt{M\{X - M(X)\}^2}$, $\sqrt{M\{Y - M(Y)\}^2}$ denoted by σ_x, σ_y are normally correlated, the coefficient of correlation ρ is defined as

$$\frac{M\{(X-A)(Y-B)\}}{\sigma_x \sigma_y} \quad \text{or} \quad \frac{M\{(X-A)(Y-B)\}}{\sqrt{M\{(X-A)^2\}} \sqrt{M\{(Y-B)^2\}}}$$

the mean values being taken for all members or pairs of values of X, Y in the doubly infinite universe.

In practice we have only a finite sample of n random pairs. Operating on the sample as we would on all the members if they were known, we have an estimate r of the true coefficient ρ , namely

$$r = \frac{\frac{1}{n}S\{(X-\bar{X})(Y-\bar{Y})\}}{\sqrt{\left[\frac{1}{n}S\{(X-\bar{X})^2\} \cdot \frac{1}{n}S\{(Y-\bar{Y})^2\}\right]}}$$

where \bar{X} , \bar{Y} denote $\frac{1}{n}S(X)$, $\frac{1}{n}S(Y)$. Change of origins and scales of measurement of the two variates does not affect r . So standardising the variates by putting x , y for $(X-A)/\sigma_x$, $(Y-B)/\sigma_y$, we have

$$r = \frac{S\{(x-\bar{x})(y-\bar{y})\}}{\sqrt{[S\{(x-\bar{x})^2\} \cdot S\{(y-\bar{y})^2\}]}}$$

With these standardised variates the joint frequency is

$$\frac{1}{2\pi\sqrt{1-\rho^2}} \exp\left\{-\frac{x^2-2\rho xy+y^2}{2(1-\rho^2)}\right\} dx dy \\ = \frac{1}{\sqrt{2\pi(1-\rho^2)}} \exp\left\{-\frac{(y-\rho x)^2}{2(1-\rho^2)}\right\} d(y-\rho x) \cdot \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{1}{2}x^2\right) dx$$

and $(y-\rho x)/\sqrt{1-\rho^2}$ and x are statistically independent standard normal variates.

Writing z for $(y-\rho x)/\sqrt{1-\rho^2}$, we have n pairs of standard normal variates (z, x) , all of which are statistically independent. Hence

$$S(z^2) = (1-\rho^2)^{-1}\{S(y^2) - 2\rho S(xy) + \rho^2 S(x^2)\} \\ = (1-\rho^2)^{-1}[S\{(y-\bar{y})^2\} - 2\rho S\{(x-\bar{x})(y-\bar{y})\} + \rho^2 S\{(x-\bar{x})^2\} + \\ n(\bar{y}^2 - 2\rho\bar{x}\bar{y} + \rho^2\bar{x}^2)]$$

which is a χ^2_n (10)

We form a set $[\xi]$ orthogonal to $[z]$ such that $S(\xi^2) = S(z^2)$ in which $\xi_1 = \frac{1}{\sqrt{n}}(z_1 + z_2 + \dots + z_n)$, and so $\xi_1^2 = \frac{n}{1-\rho^2}(\bar{y} - \rho\bar{x})^2$.

Hence from (10), writing $S_1^2 = S\{(x-\bar{x})^2\}$, $S_2^2 = S\{(y-\bar{y})^2\}$, we have

$$\xi_2^2 + \xi_3^2 + \dots + \xi_n^2 = \frac{1}{1-\rho^2}(S_2^2 - 2\rho r S_1 S_2 + \rho^2 S_1^2),$$

and this is a χ^2_{n-1} (11)

We may note by the way that as $\frac{\sqrt{n} \cdot (y-\rho\bar{x})}{\sqrt{1-\rho^2}}$ and $\sqrt{n} \cdot \bar{x}$ are statistically independent standard normal variates, therefore \bar{x} and \bar{y} are also normally correlated with coefficient ρ .

Further, as $[x]$ are statistically independent of $[z]$, we take

$$\xi_2 = \frac{1}{\sqrt{S\{(x-\bar{x})^2\}}} \{(x_1-\bar{x})z_1 + \dots + (x_n-\bar{x})z_n\},$$

which satisfies the orthogonal conditions (E.P., p. 215), whence

$$\xi_2 = \frac{1}{\sqrt{S\{(x-\bar{x})^2\}}} S\{(x-\bar{x})(z-\bar{z})\} = \frac{1}{S_1\sqrt{1-\rho^2}} S\{(x-\bar{x})(y-\bar{y}) - \rho(x-\bar{x})^2\} \\ = (rS_2 - \rho S_1)/\sqrt{1-\rho^2} \dots \dots \dots (12)$$

Hence from (11), $\xi_3^2 + \dots + \xi_n^2 = (1-r^2)S_2^2/(1-\rho^2)$, which is a χ^2_{n-2} and statistically independent of ξ_2 (13)

We have also S_1^2 as a χ^2_{n-1} and statistically independent of both ξ_2 and $(\xi_3^2 + \dots \xi_n^2)$ (14)

Thus there are three statistically independent variates :

$u = (rS_2 - \rho S_1) / \sqrt{(1 - \rho^2)}$, a standard normal variate ;

$v = \frac{1}{2(1 - \rho^2)} S_2^2 (1 - r^2)$, a Gamma variate $c \left(\frac{n-2}{2} \right)$; and

$w = \frac{1}{2} S_1^2$, a Gamma variate $c \left(\frac{n-1}{2} \right)$.

Their joint frequency is

$$\frac{1}{\sqrt{(2\pi)}} e^{-\frac{1}{2}u^2} \cdot \frac{1}{\Gamma\left(\frac{n-2}{2}\right)} e^{-v} v^{\frac{1}{2}(n-4)} \cdot \frac{1}{\Gamma\left(\frac{n-1}{2}\right)} e^{-w} w^{\frac{1}{2}(n-3)} dudvdw \quad \dots\dots\dots (15)$$

Changing the variables from u, v, w to S_1, S_2, r , the jacobian is

$$\pm \frac{1}{(1 - \rho^2)^{\frac{3}{2}}} \begin{vmatrix} -\rho & 0 & S_1 \\ r & S_2(1 - r^2) & 0 \\ S_2 & -S_2^2 r & 0 \end{vmatrix} = S_1 S_2^2 / (1 - \rho^2)^{\frac{3}{2}}$$

In terms of S_1, S_2, r the frequency element easily reduces to

$$\frac{1}{\sqrt{\pi} \Gamma\left(\frac{n-2}{2}\right) \Gamma\left(\frac{n-1}{2}\right) 2^{n-3} (1 - \rho^2)^{\frac{1}{2}(n-1)}} \exp \left[\frac{-1}{2(1 - \rho^2)} (S_1^2 - 2\rho r S_1 S_2 + S_2^2) \right] S_1^{n-2} S_2^{n-2} (1 - r^2)^{\frac{1}{2}(n-4)} dS_1 dS_2 dr,$$

and as by writing out the factorials it appears that

$$\Gamma\left(\frac{n-2}{2}\right) \Gamma\left(\frac{n-1}{2}\right) = \frac{\sqrt{\pi}}{2^{n-3}} \Gamma(n-2),$$

the constant becomes

$$\frac{1}{\pi \Gamma(n-2) (1 - \rho^2)^{\frac{1}{2}(n-1)}}$$

This is the expression for the joint frequency derived by R. A. Fisher in 1915 (16)

In the important case when $\rho=0$, ξ_2 takes a simple form and we derive directly from expressions (11) and (12) that r^2 is a Beta variate $b\left(\frac{1}{2}, \frac{n-2}{2}\right)$, or $r / \sqrt{\left(\frac{1-r^2}{n-2}\right)}$ is a t_{n-2} variate (E.P., p. 223) (17)

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THE PRODUCTION OF HYOSCYAMINE FROM DUBOISIA SPECIES.

PART I. METHODS OF QUANTITATIVE ESTIMATION.

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During a survey of plant material made with a view to the production of hyoscyamine, a need has arisen for a reliable and accurate method for determining the total alkaloid content. Considerable attention has been paid in this regard to *Duboisia* species.

Owing mainly to difficulties encountered with pigmented material, several of the published methods (British Pharmacopœia, 1932, 1936) for other drugs of the Solanaceous group, when applied to *Duboisia*, have not yielded satisfactory results in our hands. The use of larger quantities of leaf, and decinormal solutions for titration, was found to provide a degree of accuracy unobtainable in the official process of the British Pharmacopœia 1932 for *Belladonna folium*. The method submitted below has given consistent results and has been used as standard procedure in our laboratory for a considerable time.

A number of analyses carried out on the dried material by the method described are set out in the table. Results have been expressed as hyoscyamine except in those cases where the major alkaloid present has been shown to be hyoscine, i.e. in Queensland *D. myoporoides*. (Annual Report C.S.I.R., 1941-42.)

A. ESTIMATION OF TOTAL ALKALOID.

The leaf is dried in a vacuum desiccator and ground to a No. 60 powder. About 40 gms. are accurately weighed and transferred to a flask containing 200 mls. of alcohol (95%). The mixture after the addition of 10 mls. of 10% ammonium hydroxide is shaken frequently during one hour. It is then transferred to a small percolator plugged with cotton wool, packed firmly and evenly, and percolated with 95% alcohol until complete extraction of the alkaloids is effected (Mayer's test). The total time of percolation should not exceed 3 hours. The alcohol is recovered under reduced pressure at a temperature not exceeding 40° C. To the residue is added a mixture of 50 mls. of 2% sulphuric acid and 100 mls. of water, the mixture being then completely transferred to a flask. Any water-insoluble material remaining is dissolved in a small amount of alcohol (95%) and added. The acidulated solution in the flask is shaken frequently during 15 minutes and filtered, the residue on the filter being washed several times with a mixture of 10 mls. of 2% sulphuric acid and 20 mls. of water. The filtrate is transferred to a separator, 30 mls. of ether are added, the mixture shaken, allowed to separate, and the aqueous liquid reserved. The ether solution is transferred to a second separator containing 10 mls. of 2% sulphuric acid, shaken, allowed to separate, and the acid liquid added to the reserved portion. The ether is rejected. The mixed acid solutions are transferred to the first separator and the process repeated until no further colour is visible in the ether layer.

To the mixed acid solutions in the first separator, 10% ammonium hydroxide is added until distinctly alkaline, and extraction is rapidly carried out using successive portions of chloroform until complete extraction of the alkaloids is effected. The combined chloroform solutions are washed with 10 mls. of water, dried with anhydrous sodium sulphate, and filtered, the residue on the filter being washed several times with chloroform. The chloroform is then removed under

reduced pressure at a temperature not exceeding 40° C. The residue is treated with 3 mls. of absolute alcohol evaporated, and dried for 30 minutes at 100° C. Sulphuric acid (100 mls. N/10) is then added, any remaining insoluble pigmented matter being dissolved in a few drops of alcohol and added. The solution is finally made up to 250 mls. with distilled water.

A measured volume (50 mls.) of the prepared solution, with the addition of 2 drops of methyl red indicator solution, is titrated with N/10 potassium hydroxide. Duplicate determinations are carried out. Each ml. of N/10 sulphuric acid used is equivalent to 0.0289 gm. hyoscyamine or to 0.0303 gm. hyoscyne.

The above method, slightly modified, was found suitable for Duboisia Liniment of the Australian War Pharmacopoeia 1942. Where possible 200 mls. of the preparation are taken, the alcohol recovered *in vacuo* at a temperature not exceeding 40° C., and the assay completed as above, commencing with the words "To the residue is added a mixture of 50 mls. of 2% sulphuric acid . . ."

B. DECOMPOSITION OF HYOSCYAMINE.

The process submitted below for estimation of tropic acid was utilised to determine the effect of different conditions on the decomposition of hyoscyamine in aqueous solution (cf. Part II of this paper).

ESTIMATION OF TROPIC ACID.

The solution to be analysed is made acid to bromophenol blue with N sulphuric acid and extracted three times with 20% of its volume of ether. The mixed ether solutions are then washed twice with water, and the water washed twice with ether, complete separation being allowed to occur each time. The ether solutions are then combined, the ether recovered on the water bath and the residue dissolved in 10 mls. of water. Two drops of phenolphthalein solution are then added and the solution titrated with N/20 aqueous potassium hydroxide.

One ml. N/20 KOH is equivalent to 0.0083 gm. tropic acid or 0.0145 gm. decomposed hyoscyamine.

TABLE I.

Locality.	Species.	Collected.	Total Alkaloid Content w/w.
Gosford	<i>D. myoporoides.</i>	August.	2.04%
Grose River	<i>D. myoporoides.</i>	December.	1.96%
Grose River	<i>D. myoporoides.</i>	January.	2.19%
Grose River	<i>D. myoporoides.</i>	May.	1.82%
Grose River (sucker growth)	<i>D. myoporoides.</i>	—	2.59%
John's River	<i>D. myoporoides.</i>	December.	1.87%
Macquarie Pass	<i>D. myoporoides.</i>	—	1.50%
Imbil (Q.)	<i>D. myoporoides.</i>	April.	2.71%
Imbil (Q.)	<i>D. myoporoides.</i>	April.	2.91%
Yarraman	<i>D. Leichhardtii.</i>	December.	2.1%
Yarraman	<i>D. Leichhardtii.</i>	February.	1.72%
Yarraman	<i>D. Leichhardtii.</i>	March.	2.61%
Yarraman	<i>D. Leichhardtii.</i>	—	2.96%
Kingaroy	<i>D. Leichhardtii.</i>	February.	2.38%
Yarraman	<i>D. Leichhardtii.</i>	September.	1.82%
Yarraman	<i>D. Leichhardtii.</i>	November.	3.50%
Yarraman	<i>D. Leichhardtii.</i>	July.	1.77%
Yarraman	<i>D. Leichhardtii.</i>	June.	2.63%
Gosford	<i>D. myoporoides.</i>	—	1.30%

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THE PRODUCTION OF HYOSCYAMINE FROM DUBOISIA SPECIES.

PART II. EXTRACTION OF THE BASE.

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Manuscript received, July 15, 1943. Read, August 4, 1943

The nature and quantity of the major alkaloids present in the leaves of *Duboisia myoporoides* R.Br. has been shown by Barger, Martin and Mitchell (1937), and others, to vary with the locality and other factors. *Duboisia myoporoides* growing in the southern and central coastal districts of New South Wales contains hyoscyamine as its major alkaloid, whilst hyoscine predominates in trees growing in northern localities. All samples of *Duboisia Leichhardtii* F. Muell. so far examined in this laboratory contained either hyoscyamine or a mixture of hyoscyamine and hyoscine with the former predominating. Whilst fewer difficulties were encountered during the extraction of hyoscyamine from *Duboisia Leichhardtii* than from *Duboisia myoporoides*, some stands of the latter trees were found to give excellent results and are suitable for this purpose. *Duboisia myoporoides* leaves from Richmond, New South Wales, for example, were found to be more satisfactory than those collected at Gosford or Macquarie Pass.

The method adopted for the preparation of hyoscyamine is a modification of that used by Dunstan and Brown (1899) for the extraction of hyoscyamine from *Hyoscyamus muticus* Linn. The base is removed from a concentrated alcoholic extract of the leaf with water, shaken out with chloroform after the addition of ammonia, and recrystallised. Considerable variation in results was obtained during a year's experiments with *Duboisia myoporoides*.* On occasions excellent yields of pure crystalline product were obtained, whilst often the product was contaminated with a large amount of syrupy base. It is thought significant that the cleanest product was obtained from leaf collected during the autumn and winter months, whereas that collected during late spring and summer was always found unsatisfactory. It seems most probable that a seasonal variation in the nature of the bases present is operative, but this result, based on only eighteen months' work (February, 1942, to June, 1943), is subject to confirmation. The syrupy residue remaining after crystallisation of the hyoscyamine from *Duboisia* leaves collected during summer months consists largely of bases of lower molecular weight than that of hyoscyamine, and no further hyoscyamine could be obtained from the residue even on seeding.

Insufficient data on *Duboisia Leichhardtii* preclude any conclusions being drawn with regard to any such seasonal variation in this species.

Drying. Consonant with general knowledge that solanaceous drugs lose hyoscyamine if dried without control, we have found that leaves dried in direct sunshine retained only 70% to 75% of the alkaloid recoverable from leaves carefully dried in the shade until they became brittle. At best, only 70% to 75% of the alkaloids, indicated to be present by titration, could be recovered

* Grown on Cox, Findlayson & Company's Grose River farm.

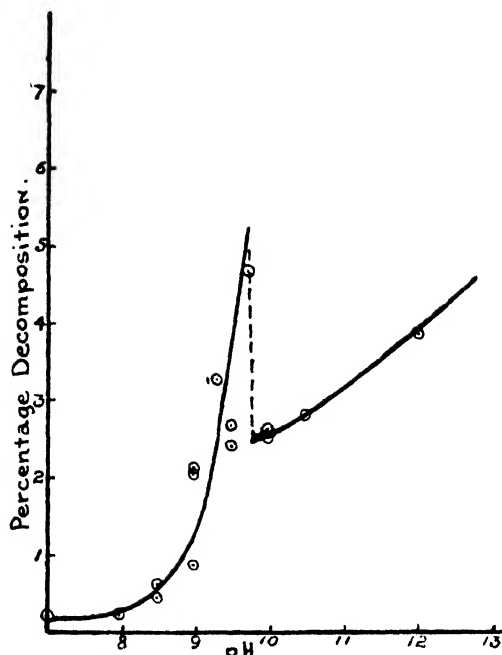


Fig 1

Hyoscyamine concentration 2%
Temp 18°C.

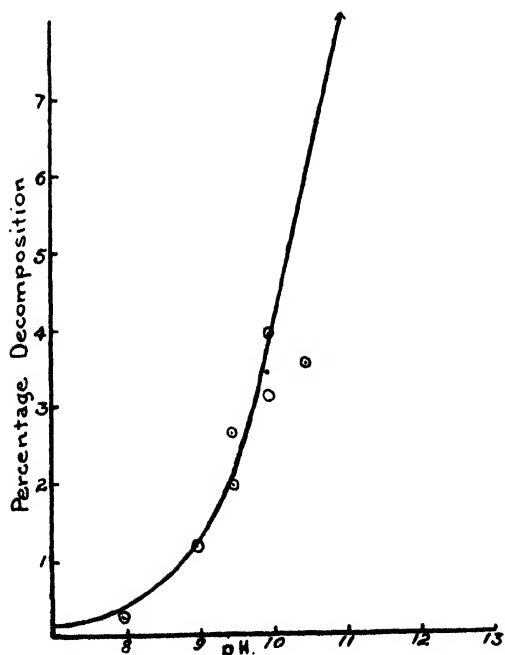


Fig. 2

Hyoscyamine concentration 1%
Temp. 18°C

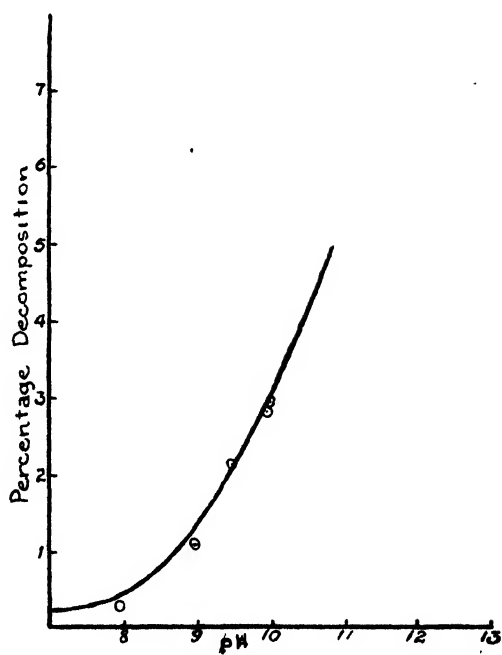


Fig. 3

Hyoscyamine concentration, 0.5%
Temp. 18°C.

Except in Fig. 4, time of reaction in each case was 5 hours.

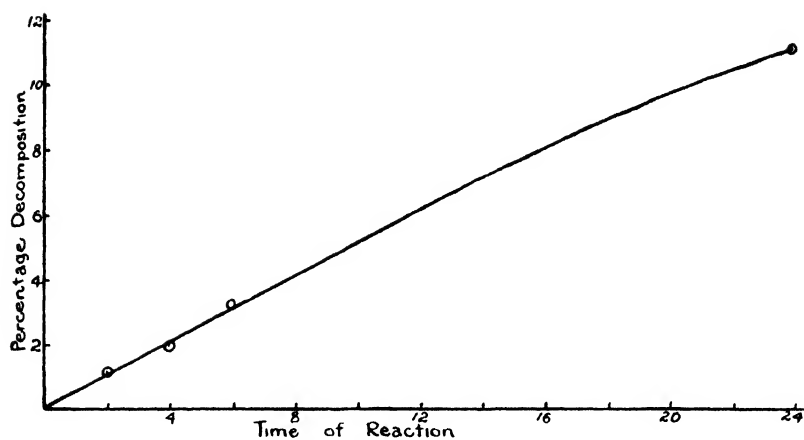


Fig 4
Hyoscyamine concentration 2% , pH 9.5 ; Temp 18°C.

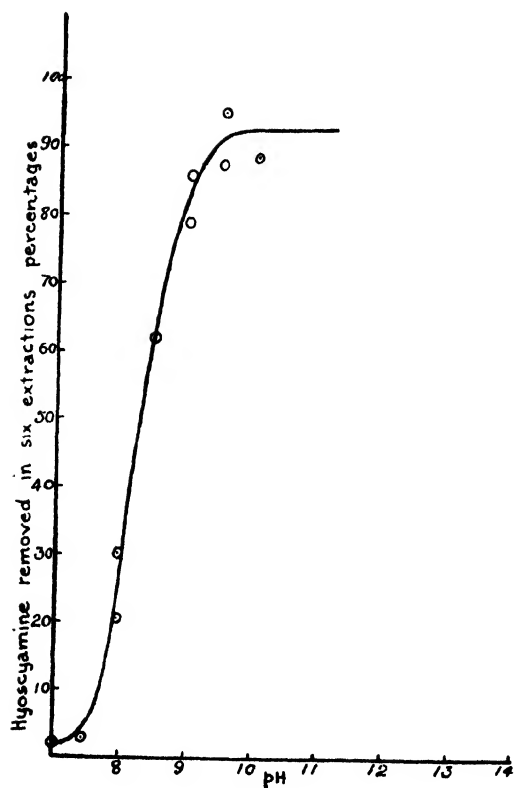


Fig. 5

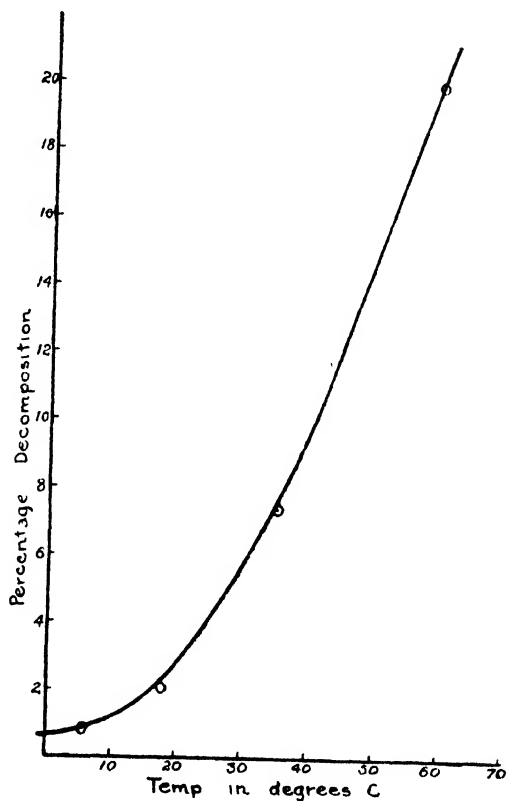


Fig 6
Hyoscyamine concentration, 2% pH 4.9

as hyoscyamine. The discrepancy is due mainly to the presence of minor alkaloids, and small losses during processing.

Alcohol Recovery. It was found that up to 20% of the recoverable hyoscyamine was lost if the alcohol recovery was carried out at atmospheric pressure. Not only is this loss avoided when reduced pressure is used, but a much cleaner product is obtained. The use of excessive steam pressures and high temperatures in the still jacket to speed up alcohol recovery leads to even greater losses of hyoscyamine.

Extraction from Aqueous Solution. The ease of extraction of hyoscyamine by chloroform from aqueous solutions is increased with increase in the pH; however, saponification of the base also proceeds at an increasing rate when the pH is raised. Experiments were carried out to determine a satisfactory pH to adopt for this extraction, so that the number of operations would be kept to a minimum commensurate with a satisfactorily low rate of saponification. Figs. 1, 2 and 3 show the amount of decomposition in a given time of different concentrations of purified hyoscyamine in alkaline solution, whilst it may be seen from Fig. 4 that this decomposition is, within limits, proportional to the time of reaction. Fig. 5 shows the increasing efficiency of the chloroform extraction with increasing pH.

These results indicate that a satisfactory pH value for chloroform extraction is from 9.0 to 9.5. If this value be not exceeded the rate of decomposition is not great, whilst the rapidity of extraction is sufficient for practical purposes.

The amount of decomposition of hyoscyamine in alkaline solution also increases with increase in temperature of the solution. From Fig. 6 it may be seen that temperatures must not be allowed to rise above approximately 20° C. if it is desired to avoid excessive decomposition of hyoscyamine.

On adding ammonia to the crude solution of hyoscyamine in water during the extraction of the base, there is often formed a finely divided brown basic precipitate. The production of this material seems to be largely dependent upon the locality from which the leaves were gathered. It has been found by experiment that no amount of rough treatment during drying will cause the formation of this brown material, but high processing temperatures seem to favour it. The removal is most troublesome and best carried out by the addition of a filter aid and filtration under vacuum.

Isolation of Hyoscyamine. The hyoscyamine is extracted from the aqueous solution with chloroform and, after purification, is crystallised from its concentrated solution in chloroform with the addition of petroleum ether.

The solvent chloroform may be removed by distillation at atmospheric pressure provided that all traces of water are first removed by treatment with anhydrous sodium sulphate. The crude base obtained is a brown, fairly viscous material which crystallises on seeding with a little hyoscyamine. The brown colouring matter, if extensive, is removed by the procedure described for recrystallising the base. It is much less soluble in a mixture of chloroform and petroleum ether than is hyoscyamine, so that on addition of petroleum ether to a chloroform solution of the base the brown viscous pigment is precipitated, and on stirring adheres to the sides of the vessel. In many cases, however, when using a satisfactory source of raw material and careful methods of extraction, this procedure is not necessary.

The crystallised hyoscyamine sometimes fulfils the requirements of the British Pharmaceutical Codex. If this is not so, however, treatment with animal charcoal or other activated charcoal in a mixture of chloroform and petroleum ether is generally sufficient to purify the product to this standard.

If hyoscyne as well as hyoscyamine is present in the leaf, separation may be effected by extraction with chloroform from the aqueous solution maintained

at a pH of about 8; advantage is thus taken of the difference in basicity of the alkaloids, as under these circumstances very little hyoscyamine is extracted. The hyoscyne may be worked up and crystallised as the hydrobromide by well-known methods.

EXPERIMENTAL.

Method of Extraction. Leaves from *Duboisia Leichhardtii* and selected *Duboisia myoporoides* trees were each successfully used for the extraction of hyoscyamine by this method. The following experiments were carried out on *Duboisia myoporoides* from near Richmond.

Shade-dried leaves practically free from stalk (360 gms.) were percolated with 90% aqueous alcohol (3.5 l.) until subsequent washings gave no positive test with Mayer's reagent. The alcohol was removed under a pressure of 60 mms. of mercury until the residue became semi-solid. The yield of soft extract was 40 gms. The alkaloid was repeatedly extracted from this material with water until the washings gave only a slight opalescence with Mayer's reagent. The use of 2% acid gives a quicker and somewhat more complete extraction but also removes extraneous basic impurities. The combined aqueous solutions (600 mls.) were treated with ammonium hydroxide until sufficiently alkaline to turn a phenolphthalein paper decidedly pink (pH 9.3). This solution, after filtration, was repeatedly extracted with approximately 5% of its volume of chloroform until all the base was removed. The combined chloroform solutions (180 mls.) were washed with water and then twice extracted with 50 mls. of 4% sulphuric acid. The acid solution of hyoscyamine was next ammoniated and extracted to completion with chloroform. The chloroform solution of crude hyoscyamine was washed with water, carefully dried with anhydrous sodium sulphate and the solvent removed by distillation at atmospheric pressure. The crude brown hyoscyamine was dissolved in a minimum of dry chloroform, light petroleum ether was added until a marked turbidity was formed, and the solution was vigorously stirred, when precipitated colouring matter adhered to the sides of the vessel. The remaining solution was decanted into a fresh beaker, a little more petroleum ether added and the whole let stand, when hyoscyamine crystallised in long needles. The crystals were filtered, washed with petroleum ether, and dried. The yield was 5 gms. or approximately 70% of the alkaloids indicated present by titration. Treatment of this product, in a mixture of chloroform and petroleum ether, with animal charcoal, followed by recrystallisation, gave a 90% yield of colourless crystals of melting point 107°–108° C., which gave an aurichloride of melting point 164° C. The specific rotation in 50% aqueous alcohol was $-21^{\circ}8$.

When hyoscyne was known to be present in the leaf, this was removed by adjusting the pH of the crude aqueous solution to approximately 8 with sodium bicarbonate or ammonium hydroxide, and extracted with chloroform. The pH was then adjusted to 9.3 in the usual fashion, and the hyoscyamine extracted.

Drying the Leaf. Two parcels each of 10 lb. of leaf from one source (Grose River, Richmond) were dried, one in direct sunlight and the other under shelter, conditions approximating to those in use in large scale practice. In the latter case the loss in weight in ten days amounted to 70.6%, the leaves were green and brittle, and contained 1.8% alkaloid as hyoscyamine. Sun-dried leaves lost 74% of their weight in six days and were coloured a decided brown, whilst the alkaloid content, as hyoscyamine, was 1.3%. A portion of each sample (500 gms.) was worked up as described, the yields of crystallised hyoscyamine amounting to 6.8 gms. (m.p. 102° C.) from shade-dried leaf and 5.1 gms. (m.p. 102° C.) from sun-dried leaf.

Recovery of Solvent Alcohol. The following experiments were carried out to decide between recovery of solvent alcohol at atmospheric or reduced pressure.

Two parcels each of 500 gms. of shade-dried *Duboisia myoporoides* leaf were percolated with 90% alcohol until exhausted, and the solvent removed, in one case at atmospheric pressure, and in the other at a pressure of approximately 60 to 100 mms. of mercury. The extract was then worked up as already described. The hyoscyamine obtained from the experiments carried out at atmospheric pressure amounted to 5.7 gms. (m.p. 98° C.) and was contaminated with a quantity of sticky basic material precipitated on addition of petroleum ether to the chloroform solution; the yield in the other instance was 6.8 gms. (m.p. 102° C.). In the former experiment a certain

amount of brown precipitated matter was formed on ammoniation of the aqueous extraction liquors, though this has been observed in greater quantity in leaf from other sources. No precipitate was formed when reduced pressure was used.

Recovery of Hyoscyamine from Aqueous Solution. Four factors were considered as possibly contributing towards the decomposition of hyoscyamine in aqueous solution, viz. (a) the pH of the solution, (b) the concentration of hyoscyamine in the solution, (c) the temperature of the solution, and (d) the time of reaction. To determine the effect of each of these variables on the rate of decomposition, solutions of hyoscyamine in dilute hydrochloric acid were prepared, and, whilst three of the factors were kept constant, the fourth was varied; the amount of decomposition was determined by estimating the amount of free tropic acid present at the end of the experiment (Lean and Ralph, 1943). The results are summarised in Table I and were used to draw the graphs 1 to 4 and 6; the discontinuity in Fig. 1 was due to the precipitation of hyoscyamine.

TABLE I.
Decomposition of Hyoscyamine in Aqueous Solution.
(pH determined with "Bayer" indicator papers.)

pH.	Concentration of Hyoscyamine. (Per cent.)	Time of Reaction. (Hours.)	Temperature Solution. ° C.	Percentage Decomposition.
7	2	5	18	0.12
8	2	5	18	0.12
8.5	2	5	18	0.6; 0.4
9	2	5	18	0.8; 2.0
9.3	2	5	18	3.3
9.5	2	5	18	2.4; 2.7
9.7	2	5	18	4.7
10.0	2	5	18	2.5; 2.6
10.5	2	5	18	2.8
12	2	5	18	3.8
14	2	5	18	27.0
9.5	2	2	18	1.1
9.5	2	4	18	1.9
9.5	2	6	18	3.2
9.5	2	24	18	10.9
10	2	2	18	1.1
10	2	4	18	2.2
10	2	6	18	2.6
10	2	24	18	11.7
9	2	5	6	1.0
9	2	5	18	2.1
9	2	5	35	7.5
9	2	5	60	20.0
9.5	1	5	18	1.9; 2.6
10.5	1	5	18	3.7
10	1	5	18	3.2; 3.9
10	0.5	5	18	2.9
12	1	5	18	20.8
14	0.5	5	18	32.0
8	1	5	16	0.2
9	1	5	16	1.2
8	0.5	5	16	0.25
9	0.5	5	16	1.0
10	0.5	5	16	2.9
12.3	1	5	16	18.0
9.5	0.5	5	16	2.1
11.9	0.5	5	16	5.8
1	1	100	16	0.4

To determine the efficiency of chloroform extraction from solutions of different pH values, solutions were prepared containing 4 gms. of hyoscyamine and sufficient ammonium sulphate, ammonium hydroxide and, if necessary, sodium hydroxide, to produce and maintain the required pH value, in 300 millilitres of water. Each solution was then extracted six times with 15 millilitres of chloroform; the base then was recovered and weighed directly. Percentages of hyoscyamine recovered are given in Table 2.

TABLE II.

Extraction of Hyoscyamine from Aqueous Solution.
(pH determined with "Bayer" indicator papers.)

pH.	Hyoscyamine Extracted.	
	Weight (gms.).	Percentage.
7	0.1	2.5
7.5	0.1	2.5
8	1.2; 0.8	30 ; 20
8.5	2.5	63
9	3.4; 3.2	85 ; 80
9.5	3.5; 3.8	88 ; 95
10	3.6	90

For pH values above 9.5 it was found that the aqueous liquors after extraction gave a negative Mayer's test even though 100% recovery of hyoscyamine was not obtained.

Evaporation of Chloroform. Previous authors have noted that the chloroform solution of hyoscyamine must be dried prior to removal of the chloroform. Our results indicate that a loss of up to 17% of the hyoscyamine is sustained if water be present in the chloroform during recovery.

ACKNOWLEDGMENTS.

The authors wish to express their thanks to the management of Cox, Findlayson & Company for permission to publish this work, and to Dr. A. Albert for much helpful criticism.

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EBONITE AS A RADIOMETER.

THE DISTORTION OF EBONITE BY LONG INFRA-RED RADIATIONS.

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Manuscript received, June 11, 1943. Read, September 1, 1943.

When one side of an ebonite strip is exposed to a greater amount of heat radiation than the other, the strip will be found to bend. Owing to its low thermal conductivity, thermal expansion will take place, mainly on the side which is irradiated, very much as is the case with a bi-metallic strip under similar conditions.

A simple and easily constructed radiometer for the detection and measurement of heat radiation has been developed by the author. This instrument is suitable for use in lieu of the usual thermo-pile and galvanometer when measuring and comparing heat radiations from different sides of a Leslie cube, for demonstrating absorption and reflection of heat radiation, and for experimental purposes, such as an experimental test of the Stefan-Boltzmann Law, etc.

Two radiometers constructed by the author on these lines are now in use for instructional purposes in the Physics Department of Sydney University.

The form of radiometer developed is illustrated in Fig. 1.

The ebonite strip E ("unloaded ebonite") is 2 cms. wide and 1.9 mm. thick. It is clamped at one end and projects 10 cms. beyond the clamp H. The surfaces of the ebonite may be rough or polished, but a rough surface when tested showed little or no advantage.

The deflections of the free end of the strip (after magnification by a factor of approximately 1,200 obtained by means of an optical lever P, as shown) are read at a distance of 1 meter from the mirror M; the latter is in the centre of a taut suspension system, between lightly twisted silk threads which provide a torsional restoring couple. O is an oil bath dipping into which are two small damping vanes B¹ and B². The radiometer should be protected from stray radiant energy, including that from the observer.

The sensitivity of the instrument described above is such that when one side of the ebonite strip is exposed to the radiation from the black surface of a 13-cm. Leslie cube, at a temperature of 90° C., and at a distance of 10 cms., a mirror scale deflection of approximately 5 cms. is obtained.

Experiments with "unloaded ebonite" strips of thicknesses varying from 0.7 to 7.5 mm. showed that within this range the thinner the ebonite the more sensitive and rapid was its response to long infra-red radiations. The thinner the strip the more is it subject to vibrational disturbance. The curves seen in Fig. 2 show the relationship between ebonite thickness and deflection on exposure to a fixed radiant energy source, e.g. a Leslie cube maintained at boiling point of water.

The zero-drift curve, Fig. 2, represents the residual reading one minute after exposure to radiation.

The instrument may be employed as a differential radiometer by exposing simultaneously one side of the strip to each of the radiant energy sources to be compared.

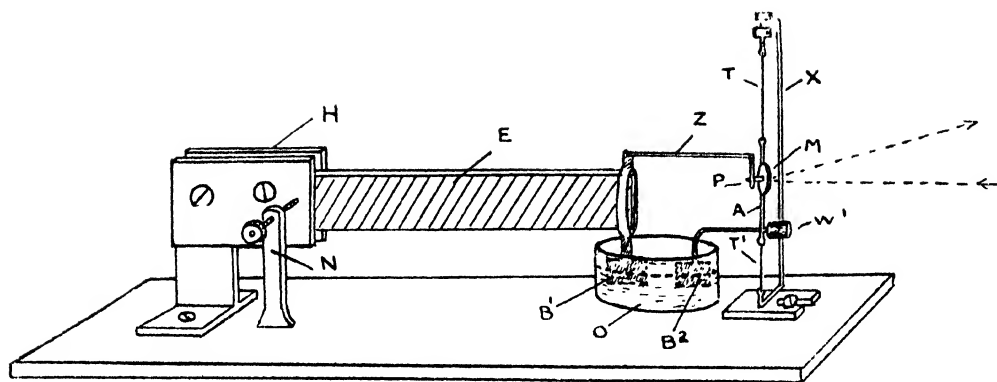


Fig. 1.

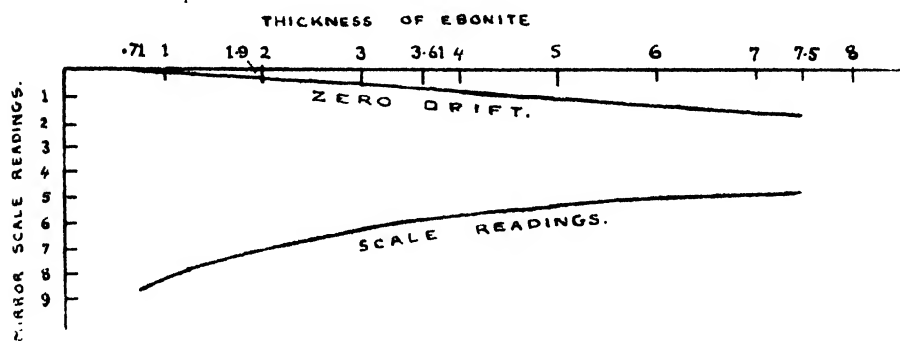


Fig. 2.

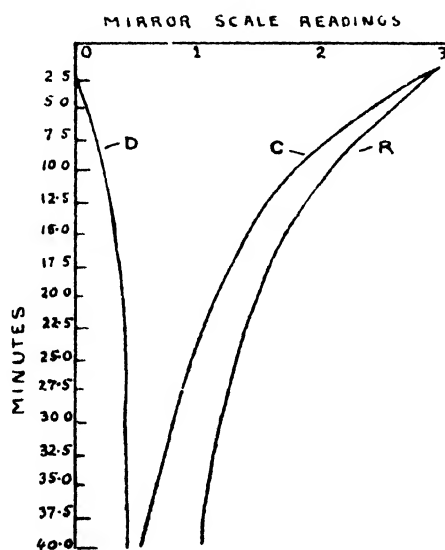


Fig. 3.

In use the entire instrument is enclosed in a box fitted with openings on one side (or on both if it is desired to use it differentially) to admit radiations, and an opening at one end for mirror illumination.

A sheet of asbestos is employed as a screen between the source of radiation and the radiometer; this is removed for each reading and then replaced.

When plotting radiation curves for a gradually cooling hot body (either temperature or time against mirror scale readings), the zero drifts are deducted from the full scale readings.

Fig. 3. Curve C is a radiation curve, after deduction of zero-drifts D from full scale readings R.

From this figure, in which the mirror scale readings are plotted against time, it will be noted that the zero-drift, though progressive, slows down as the readings proceed.

By zero-drift deduction, the radiation curve for any given radiator is still recoverable even when an unscreened radiometer is employed, and when the latter is subjected to extraneous radiations in addition to those under measurement.

It was also noted that each exposure of the ebonite to radiation produced a rapid deflection followed by a slow increase in deflection towards a maximum. On interrupting the radiation, the deflection at first rapidly decreased, and this was followed by a slow creep back to zero. It is advisable therefore to allow a short time interval between each successive reading when plotting radiation curves.

In conclusion, reference to an article by Daynes (1942) is useful. It describes the various classes of ebonite now obtainable, of which "unloaded" has the largest coefficient of expansion, and is therefore the most suitable for use as a radiometer.

This ebonite usually contains 68 parts of rubber hydrocarbon and 32 parts of sulphur, vulcanising at 140°C . "For greater flexibility and deformation at higher temperatures less sulphur is required." Therefore it is probable that a special ebonite could be made even more suitable for radiometric use.

ACKNOWLEDGMENTS.

The author wishes to thank Professor Vonwiller and members of the staff of the Department of Physics at the University of Sydney for the facilities so courteously afforded in the work associated with the development of the radiometer.

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STUDIES ON COLOUR REACTIONS FOR SUGARS.

PART I. THE IDENTIFICATION AND DETERMINATION OF MONOSACCHARIDES WITH THYMOL, HYDROCHLORIC ACID AND FERRIC CHLORIDE.

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The colour tests generally in use for the identification of sugars are tests for chemical groups of sugars such as Selivanoff's test for ketohexoses or Bial's test for pentoses. In order to identify fully an unknown sugar one has to resort to some other tests, such as the formation of crystalline derivatives, e.g. an osazone. This application of multiple tests requires a considerable amount of material which frequently is not available and sometimes is also not capable of supplying a satisfactory answer for other reasons.

In contrast to these procedures of multiple tests, the possibility was studied of using one colour test only in order to identify at least any of the commonly occurring monosaccharides. The first colour test examined may be considered to be a modification of one of the original colour tests described by Molisch in 1886 for the identification of carbohydrates in general.

Principle.

On heating, monosaccharides form with thymol in the presence of ferric chloride and hydrochloric acid deeply coloured compounds which are insoluble in water but soluble in chloroform. The colour of the aqueous suspension and of the chloroform extract and its fluorescence are characteristic of the different chemical groups of monosaccharides. In addition, individual monosaccharides are characterised by the velocity of reaction with thymol in the presence of ferric chloride and hydrochloric acid. This velocity of reaction is indicated by the varying depth of colour of the chloroform extract of the reaction mixture after different periods of heating.

Reagents.

5% solution of thymol in alcohol (95%).

0.5% solution of ferric chloride in concentrated hydrochloric acid.

Technique.

2 ml. of an aqueous solution of the monosaccharide or the substance containing it are placed in a test tube of about 1 cm. diameter together with 0.5 ml. of a 5% solution of thymol in alcohol and 5 ml. of concentrated hydrochloric acid containing ferric chloride (0.5%). After mixing the contents the tube is placed in boiling water. The water in the bath should be sufficiently deep to cover at least the height of the contents of the test tube and the bath should be sufficiently large and sufficiently heated so that the transfer of the cold test tube into it should not interrupt the boiling for more than a few seconds. During the heating the contents of the tube are observed for colour changes and the time at which they occur is noted. The changing of colour of the reaction

mixture is due to the formation of deeply coloured oils which become dispersed in the solution. If after heating for 10 minutes a definite colour change has occurred, the test tube is rapidly cooled in running cold water or in ice water. If no colour change has occurred during the first ten minutes the tube is heated further until a definite change is seen but usually for not more than 40 minutes. After cooling, a known amount of chloroform, usually 5 ml., or correspondingly less for amounts of the unknown solution under 2 ml., is added. After thorough mixing, the coloured reaction product formed dissolves readily in the chloroform. By transferring the reaction mixture and the chloroform into a larger vessel thorough mixing is facilitated.

After the two layers have separated it is in most instances possible to recognize the chemical group to which the unknown monosaccharide belongs if one examines the chloroform extract in daylight and correlates this observation with the changes observed during the heating of the reaction mixture. Confirmation and further information is gained if one examines the chloroform extract in ultra-violet light also and if one makes it alkaline with ammonia. This applies to a saccharide content of the solution tested of not less than approximately 0.05%. If it exceeds 1% observation is frequently made difficult on account of very deep colours and precipitates formed.

Results obtained by different methods of examination with pure known monosaccharides are described in the following paragraphs.

OBSERVATIONS ON PURE KNOWN MONOSACCHARIDES.

The following biologically important monosaccharides were tested with regard to their reaction with thymol, hydrochloric acid and ferric chloride:

Methyl pentose: Rhamnose.

Pentoses: Arabinose, xylose.

Ketohexoses: Fructose, sorbose.

Aldohexoses: Galactose, glucose, mannose.

A summary of the results is presented in Table I. Further details are as follows:

(a) *Observations during the Heating of the Reaction Mixture.* If a ketohexose is present a quick and intense reaction takes place. If it is present in amounts of about 0.5 mg. or more the reaction mixture takes on a deep blackish purple colour within two minutes. If present in smaller amounts an intense green

TABLE I.

	Observations during Heating.	Chloroform Extract.		
		Daylight.	Ultra-violet Light.	Ultra-violet Light and Ammonia.
Rhamnose ..	No reaction.	No colour.	Blue.	Blue.
Arabinose ..	Olive green.	Purple blue.	Dull slate blue.	Dull greenish brown.
Xylose ..				
Galactose ..	Green.	Sky blue.	Greenish blue.	Greenish blue.
Glucose ..				
Mannose ..				
Fructose ..	Quick reaction. Dark green or purple.	Dark purple.	Brilliant greenish blue.	Pale whitish blue. Pale purple blue.
Sorbose ..				

colour is produced within three minutes. One of the pentoses, xylose, reacts nearly as quickly as the ketohexoses but the colour produced is more of an olive green. The pentose arabinose, on the other hand, reacts only about half as fast as xylose. The aldohexoses galactose, glucose and mannose react approximately equally fast as arabinose which, however, produces more of an olive green colour compared with the green of the aldohexoses. If present in amounts of 0.2 mg. approximately, the aldohexoses begin to change towards green after about ten minutes of heating. With larger amounts they may change after five minutes. Generally speaking, with all monosaccharides mentioned the velocity of colour change is influenced considerably by the concentration of the monosaccharide present, but notwithstanding this it is possible to obtain considerable information with regard to which of the three groups mentioned the monosaccharide in question belongs.

No change in colour occurs even after 40 minutes of heating if the methyl pentose rhamnose is present. The reaction mixture remains yellow throughout the whole period of boiling, though it will turn cloudy as is the case with all monosaccharides and the blank.

(b) *Observations on the Chloroform Extract in Daylight.* Rhamnose does not yield a markedly coloured chloroform extract, it being practically colourless as is the blank, or only slightly yellow brown or bluish after boiling for 30 minutes or more. The aldopentoses, xylose and arabinose furnish a chloroform extract which has a typically cobalt or almost purplish blue appearance. The colour produced by xylose is about twice as intense as that produced by a similar amount of arabinose after a similar period of heating.

The aldohexoses produce in small concentration a bluish green chloroform extract. In higher concentrations (0.1% or more) it is of a sky blue colour. The chloroform extract from mannose cannot be distinguished from that of glucose by simple visual examination in any concentration, but that of galactose produces a slightly more dull blue and less intense colour than the other two aldohexoses concentrations being about equal.

The ketohexoses, fructose and sorbose, if present in amounts of 1.0 mg. or more form a deep purple chloroform extract, which can be observed readily by drawing up some of the chloroform extract into a narrow pipette. The colour of this chloroform extract, however, is not permanent and on standing for ten minutes or more it may change towards a deep blue somewhat similar to that produced by aldohexoses in high concentration. If, however, the concentration of the ketohexoses present in the reaction mixture is considerably less than 1.0 mg. then the purple colour will not be observed and a prussian blue chloroform extract will be obtained which sometimes is somewhat difficult to differentiate from that obtained from aldohexoses in higher concentration. But in conjunction with the rapid colour change in the process of heating it is possible to arrive at a definite conclusion as to whether one is dealing with a ketohexose or an aldohexose.

(c) *Observations on the Chloroform Extract in Ultra-violet Light.* At this stage of the examination, the chloroform extract need not be separated from the aqueous layer, but only the chloroform extract will give a typical fluorescence when examined in ultra-violet light in a dark room. The fluorescence obtained from a chloroform extract of a blank is a faint blue which does not materially interfere with the observations on monosaccharides.

The chloroform extract from the methyl pentose rhamnose though practically colourless when examined in daylight, fluoresces with a bright blue colour of greater intensity than that of the blank and of a darker tint. The aldopentoses, xylose and arabinose, exhibit a dull slate blue. This is in marked contrast to the much more brilliant blue fluorescence of keto- and aldohexoses. The keto-

hexoses give a strong sky blue (turquoise) fluorescence while the aldohexoses if present in about equal or even twice or three times the concentration of the ketohexoses are characterized by a less intense and more greenish blue fluorescence. If, however, the aldohexoses are present in a concentration approximately ten times stronger or more, then they show a fluorescence like that of ketohexoses.

Besides these major differences between the chemical groups some of the individual monosaccharides are characterized by variations in intensity and even in colour. For example, sorbose gives a somewhat darker blue and slightly

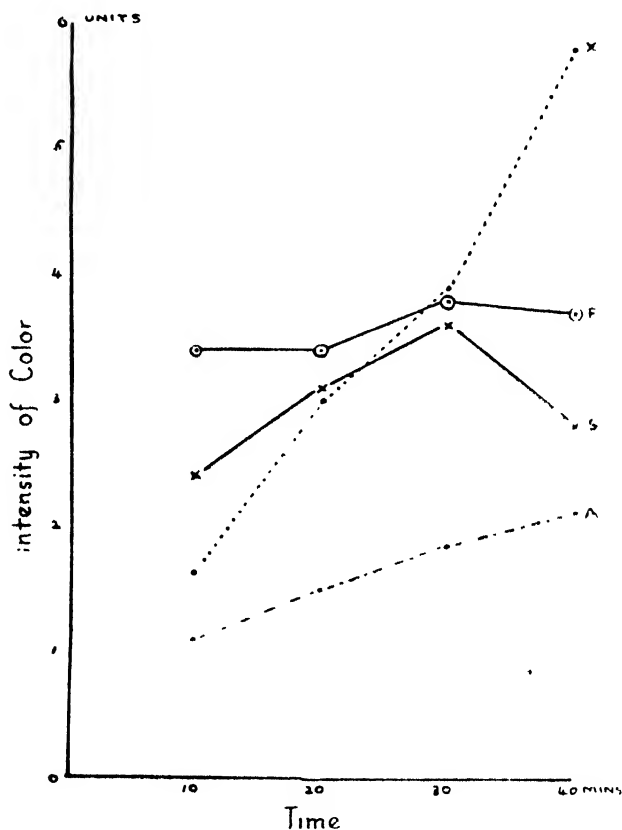


Fig. 1.—A.=Arabinose. S.=Sorbose. F.=Fructose. X.=Xylose. Intensity of colour-time curves of some aldopentoses and ketohexoses. The results were obtained with 0.01% solutions of the four monosaccharides. The measurements were made with a "Spekker" absorptiometer.

more intense fluorescence than fructose. On the other hand, when the chloroform extract resulting from these two sugars is examined in daylight, that of sorbose is distinctly lighter in colour than that of fructose, concentration and period of heating being equal. Xylose and arabinose are again distinguished by a marked difference in intensity, arabinose as also found on examination in daylight being of a lighter colour than xylose.

(d) *Observations on the Alkalinized Chloroform Extract.* The separated chloroform extract containing the reaction product is acid in reaction and if it is washed with water to remove the hydrochloric acid present it becomes pink in colour. If it is made alkaline by the addition of dilute sodium hydroxide

the aqueous layer becomes strongly green in colour while the chloroform layer assumes a slightly pink tint. These colours, however, are not stable and within a short time they begin to fade.

However, on the addition of ammonia (e.g. 1 ml. 3% ammonia for 1 ml. chloroform extract) the aqueous layer does not become coloured. The chloroform extract changes its original colour to a pink or a red, depending on the type of monosaccharide present, its concentration and the period of heating of the original reaction mixture. These differences are not very distinct, but when examined under ultra-violet light they become marked. For example, rhamnose and the aldohexoses exhibit a fluorescence similar to that seen in the acid medium. Xylose and arabinose show a dull greenish brown fluorescence which distinguishes these aldopentoses against the brilliant greenish blue fluorescences of the aldohexoses more markedly than that seen in the original acid medium.

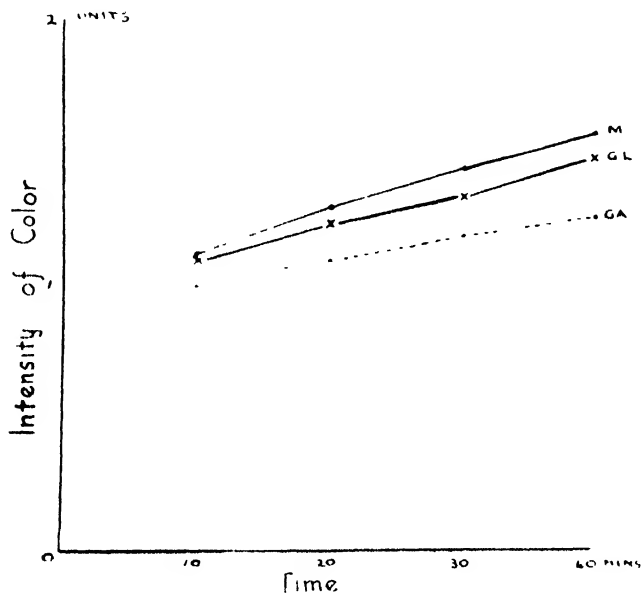


Fig. 2.—GA. Galactose. GL—Glucose. M—Mannose. Intensity of colour-time curves of three aldohexoses. The results were obtained with 0.01% solutions. The measurements were made with a "Spekker" absorptiometer.

Finally, the ketohexose, fructose, in concentrations higher than 0.05% exhibits a typically pale whitish blue fluorescence after the addition of an excess of ammonia to the deep purple freshly prepared chloroform extract. Under similar conditions sorbose exhibits a pale purple blue fluorescence. These pale fluorescences, however, are not stable and begin to change towards a deep blue on standing for ten minutes or more.

(c) *Observations on Reaction Velocity.* It has already been pointed out in this paper that the velocity of reaction varies for different monosaccharides. To determine the variation of the colour produced as a function of time, four or more test tubes containing equal amounts of the same monosaccharide and reagent are heated in a boiling water bath for ten minutes, another for twenty minutes, a third one for thirty minutes and a fourth one for forty minutes, and so on. After cooling the reaction mixtures adequate amounts of chloroform (usually 10 ml.) are added to each test tube to ensure complete extraction. After separating the chloroform layer 1 ml. of acid alcohol (prepared by the

addition of 5 ml. of concentrated hydrochloric acid to 95 ml. of absolute alcohol) are added to 9 ml. of chloroform extract in order to clarify it. Then the colour present in the extract is measured with a photo-electric colorimeter using chloroform as a blank.

The values obtained for each monosaccharide using 2 ml. of a 0.01% solution for each test are shown in Fig. 1 and 2 in the form of time curves. They demonstrate that some of the individual monosaccharides are characterized by typical curves. For example, xylose forms a much steeper curve than arabinose. Fructose and sorbose also yield curves which are typical for each of the two ketohexoses, sorbose reacting slower and giving a less intense colour than fructose (Fig. 1). In the case of the aldohexoses the picture is less favourable, glucose and mannose forming very similar curves. Galactose, however, furnishes a definitely different colour-time curve (Fig. 2). Rhamnose, of course, is characterized by the fact that practically no reaction takes place.

Sorensen and Haugaard (1933) studied the velocity of reaction between a number of monosaccharides and orcinol and sulphuric acid. In their case the reaction has to be carried out at exactly 85° C. The resulting time curves from some of the monosaccharides tested (xylose and arabinose, fructose and sorbose) lie very close together. Moreover, the blank is not colourless and there seems to be no possibility of removing interfering colours from the aqueous reaction mixture.

THE DETERMINATION OF AN UNKNOWN MONOSACCHARIDE.

When dealing with an unknown monosaccharide it is advisable to determine first the chemical group to which it belongs. This can readily be accomplished by performing the reaction as described and by observing the colour of the chloroform extract before and after alkalization in daylight and in ultra-violet light. The colours produced by the unknown should, if possible, be compared with those obtained under similar conditions from known monosaccharides in order to facilitate their recognition. If using similar amounts for standard and unknown, some individual monosaccharides such as fructose and sorbose may readily be recognized also at this stage, while in other instances it will be necessary to determine the velocity of reaction for this purpose. In this instance again the concentration of the unknown should preferably be about the same as that of the known. The correct concentration which should not differ by more than 50% from that of the known can be determined by preliminary experiments, for example, when determining the chemical group to which the unknown belongs.

The velocity curves shown in this paper were obtained with concentrations of 0.01% or 0.2 mg. of monosaccharide for each test tube. Such a concentration will be found to be satisfactory though for aldohexoses a concentration of about 0.02% may be found to be preferable.

While performing this qualitative test it is also possible to determine quantitatively the amount of monosaccharide present simply by comparing the colour of the chloroform extract with that of a standard of the identical monosaccharide similarly treated.

SUMMARY.

A simple colour reaction of monosaccharides with a reagent consisting of thymol, ferric chloride and hydrochloric acid, has been described.

By observing the water-insoluble reaction product and its solution in chloroform in daylight and in ultra-violet light, it is possible to recognize the chemical group such as aldopentose, methyl pentose, aldohexose and ketohexose

to which the monosaccharide belongs. Individual monosaccharides such as fructose and sorbose may also be recognized at this stage.

Individual monosaccharides differ in velocity of reaction and utilization of this easily ascertained gradient enables one to differentiate between the members of a chemical group of monosaccharides.

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THE CHEMISTRY OF BIVALENT AND TRIVALENT IRIDIUM.

PART I. COMPOUNDS OF BIVALENT IRIDIUM HALIDES WITH TERTIARY ARSINES.

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and R. S. NYHOLM, M.Sc.

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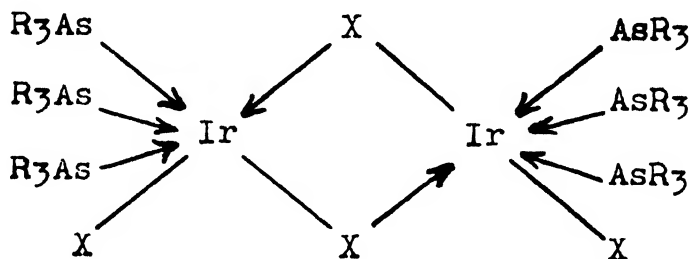
Compounds of bivalent iridium appear to be as rare as those of bivalent rhodium, the only simple salt described being apparently the chloride, obtained by the pyrolysis of the trichloride, which at higher temperatures is claimed to yield the monochloride. (Wohler and Streicher, 1913.) A series of alleged ammines prepared by Skoblikoff (1885) have been shown by Palmaer (1895) to be in reality compounds of trivalent iridium, whilst the single compound $2\text{IrCl}_2 \cdot 3(\text{C}_2\text{H}_5)_2 \cdot \text{S}_2$, prepared by Ray and Adikari (1932) by heating iridium trichloride with dimethyl sulphide in alcoholic solution, cannot be formulated according to the usual coordination formulæ, and merits further study. From preliminary tests by the present authors, it does not appear that alkyl sulphides are capable of effecting the necessary reduction from the trivalent to the bivalent state.

As with the corresponding rhodium compounds (Dwyer and Nyholm, 1941) the coordinated bivalent iridium complexes described in this paper have been prepared by reduction with hypophosphorous acid of the trivalent complexes prepared *in situ*. Like rhodium, simple trivalent or tetravalent iridium salts were readily reduced in acid solution to a very pale orange yellow solution in which the metal was present in the bivalent state, as a hypophosphite of considerable stability, since no coordination compounds could be prepared from such prereduced solutions, nor could the metal be precipitated even on prolonged boiling.

A series of well-defined tris arsine complexes $\text{IrX}_2 \cdot 3\text{AsR}_3$ and two poorly defined tetrakis complexes $\text{IrX}_2 \cdot 4\text{AsR}_3$ have been isolated. The tris complexes, although of lower stability than the corresponding rhodium compounds, were weakly coloured solids, poorly crystalline except the bromide, with relatively low melting points, insoluble in water, but easily soluble in organic solvents. In alcoholic solution they reduced silver nitrate to the metal even at room temperature but gave no precipitate of the silver halide except on prolonged boiling. The superior reducing power of the bivalent iridium complexes over the bivalent rhodium is to be expected. Although the tris compounds are probably dimeric in the solid state (I), unlike the rhodium compounds, they are dissociated in boiling chloroform or freezing benzene.

In the rhodium series (Dwyer and Nyholm, 1942) stable monomeric covalent tetrakis arsine complexes were prepared with the bromide and the iodide, but with iridium the tetrakis compounds always had an odour of arsine, and they could be transformed easily to the tris compounds by shaking with petroleum ether. However, from their extreme solubility in organic solvents and their failure to precipitate the silver halide except on prolonged boiling with alcoholic silver nitrate, it is concluded that they are to be formulated $\text{IrX}_2 \cdot 4\text{AsR}_3$.

As a result of the experiments with iridous bromide, which gave the most stable complexes, and by varying the proportions of arsine to iridium, it is concluded that only the tris and tetrakis compounds are formed, and hence that bivalent iridium, in the arsine series at least, has a coordination number of six.



EXPERIMENTAL.

Hexakis-diphenylmethylarsine-μ-dichlorodi-iridium. I. Sodium hexachloriridate solution (10 mls.) containing 0.123 g. iridium was reduced to the trivalent state by refluxing with alcohol (10 mls.) and concentrated hydrochloric acid (10 mls.) until the colour changed to olive green. Diphenylmethylarsine (0.47 g.) was then added, followed by alcohol sufficient to produce one phase on heating. The mixture was refluxed for a few minutes to form the trivalent compound and then 30% hypophosphorous acid (3 mls.) was added and the mixture refluxed for 50 minutes. The resulting pale yellow solution was cooled, precipitated with water, and allowed to stand, when a yellow oil separated, which was purified by solution in alcohol, reprecipitation with water, and finally addition of a little petroleum ether. The resulting very pale yellow microcrystalline powder, m.p. 115–116° C., was very soluble in organic solvents such as benzene and chloroform. An alcoholic solution reduced silver nitrate to the metal at room temperature.

The substance was analysed for iridium by ignition, followed by heating in a reducing atmosphere, and for the halogen as described previously for the rhodium compounds. In this compound high results were always obtained for the halogen owing to oxidation during purification.

Found: Ir=19.3%; Cl=8.9%; calculated for $(IrCl_2 \cdot 3(C_6H_5)_2AsCH_3)_2$, Ir=19.38%; Cl=7.13%.

Hexakis-diphenylmethylarsine-μ-dibromo-di-iridium. I. This was prepared as with the chloride above, substituting hydrobromic acid (49%) for the hydrochloric acid. After about 30 minutes' refluxing a bright yellow precipitate came down, and the reaction was stopped when the bumping had become extremely violent. The resulting compound after washing with aqueous alcohol was dried in a desiccator over sulphuric acid. The substance crystallised in short thick rods m.p. 245° C. with decomposition. It was soluble in hot acetone, sparingly soluble in hot alcohol, but soluble in cold chloroform or benzene, and precipitated from the latter solvent by petroleum ether.

Found: Ir=17.6%; Br=14.7%. Mol. wt. (ebullioscopic in chloroform), 864, 816; (cryoscopic in benzene) 811.

Calculated for $(IrBr_2 \cdot 3(C_6H_5)_2As(CH_3)_2)_2$: Ir=17.79; Br=14.74; mol. wt.=2,170.

Hexakis-diphenylmethylarsine-μ-diiodo-di-iridium. I. The iridium solution (10 mls.) as before was treated with potassium iodide (2 g.) and boiled until iodine ceased to be evolved. The arsine and alcohol was added to the light brown solution of iridium triiodide and finally the reducing agent, as before. After refluxing for 40 minutes, the solution was treated with water and cooled, when it gave a brownish yellow microcrystalline powder, m.p. 80–82° C. The compound reduced silver nitrate to the metal and was soluble in organic solvents.

Found: Ir=16.25%; I=21.8%; calculated for $(IrI_2 \cdot 3(C_6H_5)_2As(CH_3)_2)_2$: Ir=16.33%; I=21.54%.

Hexakis-dimethyl-p-tolylarsine-μ-dichloro-di-iridium. I. This compound, prepared in the same manner as the chloride above, gave an oil which was induced to crystallise by treatment with petroleum ether at low temperatures. It was fairly soluble in petroleum ether, and easily soluble in benzene and chloroform, and reduced silver nitrate to the metal. The very pale yellow powder melted at 97° C.

Found: Ir=21.9%; calculated for $(\text{IrCl}_2 \cdot 3(\text{CH}_3)_2\text{As}(\text{C}_7\text{H}_7))_2$; Ir=22.66%.

Hexakis-dimethyl-p-tolylarsine-μ-dibromo-di-iridium. I. Prepared as before, this gave a yellow microcrystalline powder, difficult to obtain solid, m.p. 96° C. The substance was easily soluble in alcohol, acetone and benzene.

Found: Ir=20.5%; Br=17.2%; calculated for $(\text{IrBr}_2 \cdot 3(\text{CH}_3)_2\text{As}(\text{C}_7\text{H}_7))_2$; Ir=20.53%; Br=17.00%.

Hexakis-dimethyl-p-tolylarsine-μ-diiodo-di-iridium. I. Prepared as with the iodide above, the complex with this arsine was precipitated with water, coagulated with a little petroleum ether, washed with aqueous alcohol and dried over concentrated sulphuric acid. The substance melted at 86–88° C, was easily soluble in alcohol, acetone or benzene and reduced silver nitrate to the metal at room temperature.

Found: Ir=18.7%; I=24.9%; calculated for $(\text{IrI}_2 \cdot 3(\text{CH}_3)_2\text{As}(\text{C}_7\text{H}_7))_2$; Ir=18.65%; I=24.54%.

Tetrakis Compounds. A number of attempts were made to prepare these compounds using dimethylphenylarsine and dimethyl-p-tolyl-arsine, which readily gave this type of compound with rhodium. Using iridium bromide and four moles of the arsine under the usual conditions, two oily yellow substances were obtained, which became solid after trituration with petroleum ether. The yellow solids had a powerful odour of arsine, were very readily soluble in organic solvents, and on treatment with alcoholic silver nitrate gave no precipitate of the halide except on prolonged boiling. On analysis they appeared to be mixtures of the tris and tetrakis compounds, and on further treatment with petroleum ether the percentage of tris compound increased, indicating loss of arsine from the tetrakis compound.

Found: Ir=16.5%; calculated for $\text{IrBr}_2 \cdot 4(\text{CH}_3)_2\text{As}(\text{C}_7\text{H}_7)$; Ir=16.97%.

Found: Ir=19.53%; calculated for $\text{IrBr}_2 \cdot 4(\text{CH}_3)_2\text{As}(\text{C}_6\text{H}_5)$; Ir=17.87%. (The tris compound required Ir=21.47%.)

SUMMARY.

The preparation of a number of bivalent iridium halides stabilised with tertiary arsines is described. The compounds are probably dimeric, with halogen bridges, and act as powerful reducing agents towards silver nitrate solution.

ACKNOWLEDGMENT.

The authors are indebted to Mr. D. P. Mellor for suggesting the problem of preparing bivalent iridium compounds and also for specimens of potassium chloro-iridate.

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 Sydney Technical College.

STRINGOCEPHALID BRACHIOPODA IN EASTERN AUSTRALIA.

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With Plates IV, V and three text-figures.

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1. INTRODUCTION AND SUMMARY.

Brachiopods of the Middle Devonian family Stringocephalidae are known to occur in two provinces in eastern Australia, one in north Queensland, in the Burdekin River District south of Townsville; the other in New South Wales, near Attunga, in the Tamworth District.

The genus *Stringocephalus* was first recorded from Australia by R. Etheridge, Junr. (1892, p. 67), who doubtfully referred a single specimen from the Fanning Limestone, Queensland, to this genus. Later, W. S. Dun (1900, p. 195) recorded from Crawney, N.S.W., "*Brachiopoda*, indet.", which W. N. Benson (1922, p. 178) listed as "*Stringocephalus* (?) sp. indet." The latter specimens (G.S. 4845, 4862, 4866) are in the Geological Survey Collection, Sydney, but are not available at present.

The present paper is based on two collections: (1) from north Queensland, from Fanning River and from Reid Gap, 31 miles south of Townsville, and (2) from north of Sulcor Quarry, 4 miles north of Attunga and 17 miles north of Tamworth, N.S.W.

The Queensland specimens prove to be indistinguishable from *Stringocephalus burtini* Defrance of the upper Middle Devonian (Givetian) beds of Paffrath, Germany. In Queensland, the associated fossils are *Atrypa* spp. (possibly new species), *Gypidula* sp. (= *Pentamerus brevirostris* of Etheridge, 1892, p. 67, Pl. 37, figs. 9-11), *Amphipora* sp., *Favistella rhenana* (Frech) and other Rugose corals.

The presence of *Stringocephalus* has not been proved in New South Wales. Large brachiopods from Attunga, showing some external resemblances to *Stringocephalus* and erroneously referred to that genus (Brown, 1942), prove to be *Bornhardtina*. This form is closely related to *Stringocephalus* both morphologically and stratigraphically.

Near the north-eastern corner of Portion 115, Parish of Burdekin, in the Attunga district, *Bornhardtina* forms a shell-bank or bioherm, which occurs between biostromes of *Amphipora* sp. (? *A. ramosa*). A small Rugose coral (*Favistella* sp.) occurs in the Brachiopod limestone.

The writer is indebted to Mr. and Mrs. E. D. Coulter of Attunga for kindness and hospitality during the course of field-work, and gratefully acknowledges a grant covering field-expenses from the Commonwealth Research Fund administered by the University of Sydney.

She has to thank Dr. Dorothy Hill for making possible the loan of all the material from the Queensland localities, and Mr. L. L. Waterhouse, of the Geology Department, University, for the loan of photographic apparatus.

2. STRATIGRAPHICAL CONSIDERATIONS.

In the standard Devonian sequence near Cologne, in the Rhine Valley, Germany, the Middle Devonian is divided into the *Calceola* Stage (Eifelian or JJ—October 6, 1943.

Couvinian) below, and the *Stringocephalus* Stage (Givetian) above. (Tilman *et al.*, 1938.) The maximum development of *Stringocephalus* appears to be in the upper part of the Middle Devonian, where it is accompanied by *Rensselandia* (*Newberria*) *caiqua* (d'Archiac and Verneuil) and *Amphipora ramosa* (Phillips). *Stringocephalus* also occurs in the Middle Devonian limestones of the south of England, especially near Torquay and Plymouth. (Davidson, 1853, 1864.)

Bornhardtina occurs in the lower part of the *Stringocephalus* Stage (the Upper Honsel or *quadrigeminus* beds) of the Paffrath Basin at Gerolstein, Germany.

In North America, *Stringocephalus* was first recognised by Whiteaves (1890), 1891, as occurring in western Canada. Kirk (1927) recorded its occurrence in Prince of Wales Island, Alaska, and also in Nevada and Utah. Other occurrences are recorded by Cooper *et al.* (1942). Dr. Cooper discusses the evidence of the stratigraphical horizon of the *Stringocephalus* beds and concludes: "This evidence suggests that the American and Canadian occurrences represent a single zone. The writer knows no contradictory evidence and has therefore placed all the *Stringocephalus* occurrences as equivalent and low in the Givetian."

A. W. Grabau (1931) and C. C. Tien (1938) have described *Stringocephalus* as occurring abundantly in the provinces of Hunan and Yunnan in southern China. Several mutations of *Stringocephalus burtini* are present, and these are shown by Tien (1938, p. 13) to occur on two horizons, *S. burtini* at the top of the Chitzechiao Limestone, and *S. burtini* mut. *alpha* Grabau and *S. burtini* mut. *beta* Tien in the underlying Ichiawan Shale.

These beds represent the upper part of the Middle Devonian Series as developed in southern China, and are equivalent to the Givetian of Europe. (Tien, 1938, p. 6.) The associated brachiopods are *Meristella* spp., *Atrypa* spp., *Athyris aspera* and *Ambocoelia sinensis*.

In Australia, the occurrence of *Stringocephalus* in the Fanning River and Reid Gap Districts, Queensland, proves the existence of rocks of Givetian age, and this is confirmed by the presence of Rugose corals, shown by Dr. Dorothy Hill (1942) to be either identical with or closely related to species in the *quadrigeminus* and Büchel beds of the Paffrath Basin.

The writer's work in the Tamworth District, New South Wales (Brown, 1942) was originally undertaken with the object of correlating the limestones there with extra-Australian occurrences. The age of the *Sanidophyllum* fauna in the Moore Creek limestone has been one of the problems of Devonian stratigraphy ever since the fauna, largely endemic, was described by Etheridge in 1899. The discovery of a clear sequence of fossiliferous limestones in the hills north of Sulcor Quarry established the relative positions of the Murrumbidgee (=Sulcor) and Moore Creek faunas. The identification of *Bornhardtina*, one of the *Stringocephalidæ*, in the lower part of the Moore Creek Limestone, below the *Sanidophyllum* zone, now definitely fixes the age of the Brachiopod Limestone as Lower Givetian (=Upper Honsel of Paffrath Basin), and by inference, places the underlying Sulcor Limestone (=Murrumbidgee) in the Couvinian or lower part of the Middle Devonian.

The Tamworth sequence is shown diagrammatically in the accompanying columnar section.

3. SYSTEMATIC DESCRIPTIONS.

The terminology used in the following descriptions is that of Allan Thomson (1927), Muir-Wood (1936) and Ulrich and Cooper (1938), where applicable. Definitions of the terms are tabulated by Cloud (1942).

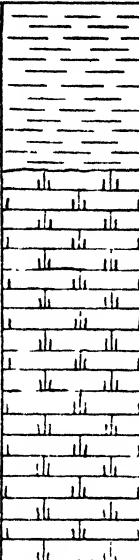
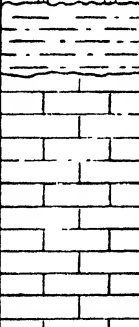
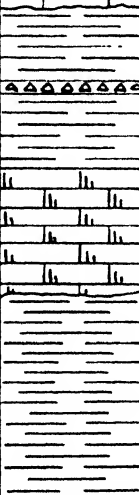
European Stages	Tamworth Series, Attunga, N.S.W.		
Middle Devonian Givetian	Moore Creek Stage		<p>Radiolarian Cherts</p> <p>Moore Creek Limestone</p> <p>Zone of <i>Sanidophyllum davids</i>, <i>Spongophyllum giganteum</i>, <i>Disphyllum robustum</i>, <i>Phacellophyllum porteri</i>, <i>Mesophyllum cornubovis</i>, <i>Syringopora porteri</i>, <i>Heliolites porosa</i>.</p> <p>Zone of <i>Stringophyllum bipartitum</i>, <i>Sanidophyllum colligatum</i>,</p> <p>Zone of <i>Bornhardtina coulteri</i>, <i>Favistella cf. rhenana</i>, <i>Amphipora</i> sp.</p>
Couvinian	Sulcor Stage		<p>Cherts and Tuffs</p> <p>Sulcor Limestone</p> <p><i>Eridophyllum bartrumi</i>, <i>Receptaculites australis</i>, <i>Phillipsastraea maculosa</i>, <i>Prismatophyllum brownæ</i>, <i>Pseudamplexus princeps</i>, <i>Trapezophyllum coulteri</i>, <i>Xystriphyllum mitchelli</i>, <i>Syringopora speleana</i>, <i>Syringopora</i> spp., <i>Stromatoporella loomderensis</i></p>
Lower Devonian Coblenzian	Nemingha Stage		<p>Cherts and Tuffs with band of limestone-breccia</p> <p>Nemingha Limestone <i>Acanthophyllum cf. mansfieldense</i>, <i>Xystriphyllum insigne</i>, <i>Lyrulasma floriforme</i>, <i>Lisophyllum konincki</i>, <i>Syringopora</i> spp.</p> <p>Cherts and Tuffs</p>
Gedinnian			

Fig. 1.—Diagrammatic columnar section of the Tamworth Series near Attunga, N.S.W., to show the position of the *Bornhardtina* zone. Vertical scale approximately 100 ft.=1 in.

Class BRACHIOPODA Duméril.

Order TELOTREMATA Beecher, 1891.

Super-family Terebratulacea Waagen, 1883.

Family Stringocephalidæ King, 1850.

1850. King, W., Palæontog. Soc. Monogr., The Permian Fossils of England, p. 141.

1942. Cloud, P. E., Geol. Soc. Amer., Special Paper, No. 38, p. 91.

"Large, thick shelled, generally unornamented terebratuloids with discrete hinge plates and a long marginal loop with modified crural points. Dental plates obsolete or obsolescent. Median septa and cardinal process present or absent. Deltidial plates discrete or conjunct. Foramen hypothryd to permesothyrid.

"Geologic Range: Middle Devonian of the Northern Hemisphere. This family is so characteristic of the Middle Devonian that the presence of any of its members is presumptive evidence of that age for the beds involved." (Cloud, p. 91.)

Sub-family Stringocephalinæ Cloud, 1942.

Genus Stringocephalus Defrance, 1825.

1824. Defrance, Tabl. Corps Org. Foss., p. 110 (no description).

1825. Defrance, in Blainville, Manuel de malacologie et de donchyliologie, text (1825), p. 511; atlas (1827), Pl. 53, f. 1-1c.

1827. Defrance, Dict. Sci. Nat., Vol. 51, p. 102, pl. 75.

1842. Sandberger, Leonhard und Bronn's Jahrb. für Mineralogie, p. 386.

1942. Cloud, P. E., Geol. Soc. America, Special Paper, No. 38, p. 104 and refs.

For further discussion of the genus see Davison (1853, 1864), Hall and Clarke (1893), Torley (1908), R. Wederkind (1917, 1925), A. W. Grabau (1931), T. H. Ting (1936) and C. C. Tien (1938).

Genotype (by original designation): *Terebratula burtini* = *Stringocephale burtini* Defrance, 1825.

Diagnosis (after Cloud, 1942): "Large, subglobular to transversely sub-lenticular Stringocephalidæ. Beak prominent, deltidial plates conjunct in adults, foramen hypothryd, ventral interarea or planareas present and ordinarily well developed. Having prominent median septa in both valves and a long rod-like, terminally bifid cardinal process in the dorsal valve. Hinge plates discrete, not supported by crural plates."

Geological Range: Upper Middle Devonian of the Northern Hemisphere.

Stringocephalus burtini Defrance, 1825.

Plate IV, Figs. 1-6, text-figure 1.

Holotype (Chosen Cloud, 1942, p. 108): Specimen represented by Fig. 1a in Plate 53 in original illustrations by Defrance (in Blainville, 1827, *loc. cit.*). Refigured by Cloud, 1942, Plate 18, fig. 6.

Locality: Paffrath, Germany.

Diagnosis: As for the genus.

Australian Material and its Preparation: The fossils from Queensland are replaced by white, crystalline calcite and are embedded in massive, black limestone, from which it is extremely difficult to obtain complete specimens.

One specimen (Q.U. Coll. F.6977) from Ryan's Quarry, Calcium, Reid Gap (Plate IV, figs. 1-3) was naturally weathered to reveal an internal mould showing the pallial markings and septa. Both beaks were preserved as replacements in crystalline calcite and black limestone matrix occurred between the beaks.

Careful removal of the matrix by means of an automatic percussion chisel revealed on the ventral valve the interarea, the concave deltidial plates and the foramen.

Another incomplete specimen (Q.U. Coll. F.6976) embedded in black limestone from the same locality was sliced vertically along the median plane of symmetry; one-half of this specimen was ground parallel to this plane, and a series of *camera lucida* drawings is reproduced in text-figure 2: a wax scale-model, constructed from these drawings in the manner described by St. Joseph (1938) (Plate IV, figs. 4-5) revealed several important internal characters.

Description: Exterior. Shell large, sub-globose; lateral profile bi-convex; immature specimens are relatively long, but older specimens are as wide as long; measurements of three specimens from Queensland are compared with those of typical specimens from Paffrath, Germany, and from China in the accompanying table.

Measurements of *Stringocephalus burtini* (in mm.).

Column	I.	II.	III.	IV.	V.	VI.	VII.
Height of ventral valve ..	80	72	67	69.0	69.5	40	85
Height of dorsal valve ..	65	56	61	57.1	55.5	30	72
Width	72	83	62	61.0	74.7	35	80
Thickness	60	45	47	43.0	—	25	56
Umbonal angle V.V. ..	—	115°	100°	113°	103°	—	—
Umbonal angle D.V. ..	—	160°	160°	160°	155°	—	—
Length of hinge line ..	—	36	22	18.5	51	—	—

- I. Queensland Univ. Coll. F.6976, sectioned specimen. Loc. Ryan's Quarry, Por. 62v, Par. Wyoming, Q. (Calcium, Reid Gap.)
- II. Queensland Univ. Coll. F.6977, specimen figured Pl. A, figs. 1-3. Loc. as for I.
- III. Queensland Univ. Coll. F.6978. Loc. as for I.
- IV. Topotype in Sydney Univ. Coll. 2480. Loc. Paffrath, Germany.
- V. Mansuy's Specimen, quoted Grabau, 1931, p. 525. Loc. Yunnan, China.
- VI. Original type of DeFrance (Chosen Cloud, 1942). Approximate measurements of immature specimen, Paffrath, Germany. (Cloud, p. 108.)
- VII. Dimensions of average adult, quoted Cloud, p. 108.

Anterior commissure rectimarginate; cardinal margin submegathyrid, hinge slightly less than half the width of the shell. Beak of the ventral valve high, erect in immature specimens, incurved in older specimens, with an umbonal angle of 115 degrees. The ventral interarea is relatively high, being about 15 mm. high and about 50 mm. wide, orthocline to anacline, divided medially into two triangular regions by concave, conjunct deltidial plates, which together are 30 mm. wide along the hinge-line. The foramen is marginally hypothryid in position (Plate IV, fig. 1). The beak of the dorsal valve is inconspicuous; the dorsal palintropes are not visible from the outside but appear in the scale model as narrow areas, radiating from the beak. Surface smooth, without trace of fold or sulcus. Shell substance thick posteriorly (ca. 10 mm.), becoming thinner anteriorly; the structure of the shell is obscured by recrystallisation.

Interior: In the ventral valve dental lamellæ are absent and the hinge-teeth, about 40 mm. apart, are free, short and curved upwards and inwards in the manner characteristic of the genus and of the Terebratulacea generally. A double median septum is present (Q.U. Coll. F.6978) extending two-thirds of the distance from the beak to the anterior margin. Muscle-scars (?) and radially arranged vascular markings appear in the cast of specimen Q.U. Coll. F.6977. (Plate IV, fig. 1.)

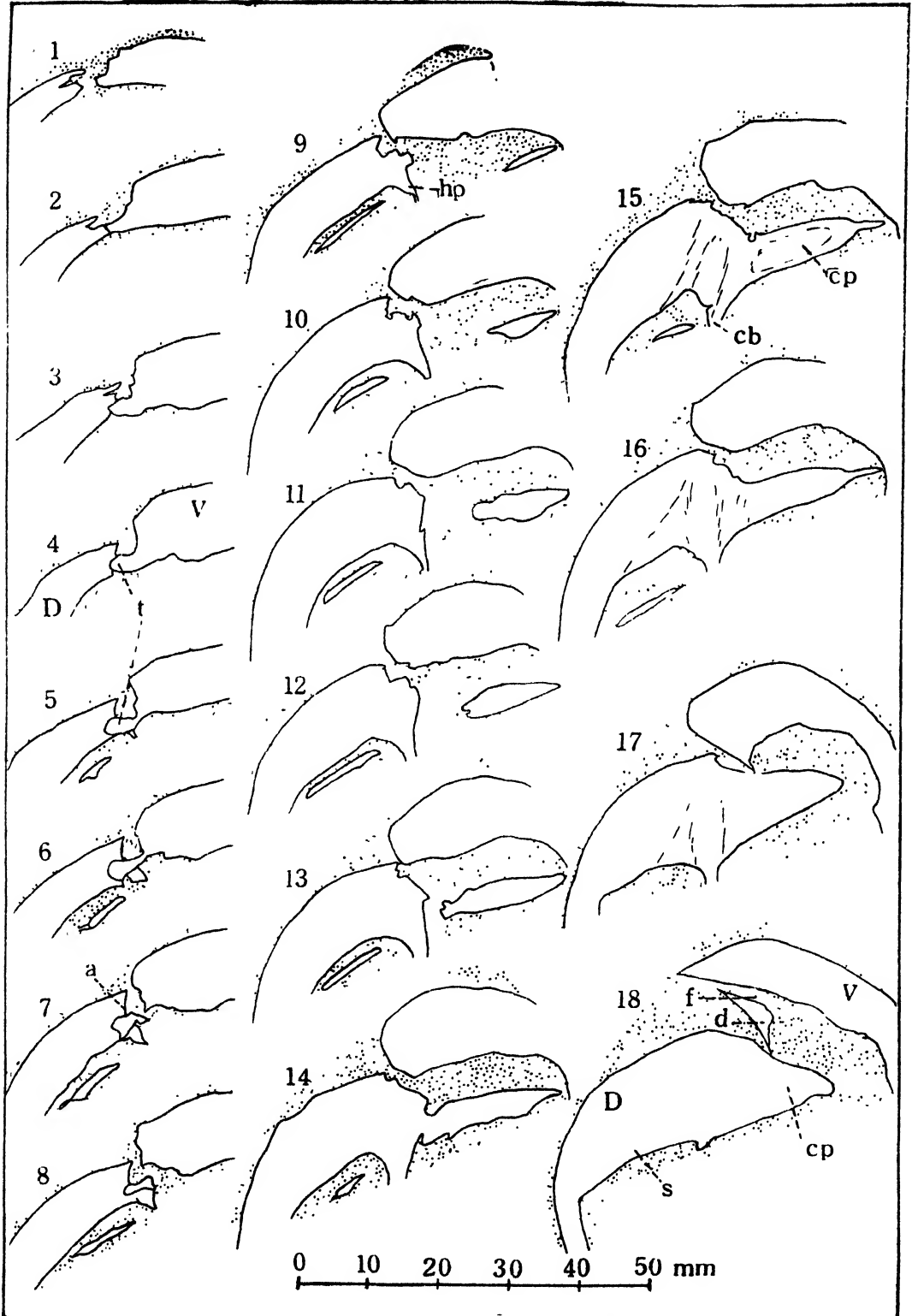


Fig. 2.—Serial sections through *Stringocephalus burtini* from Calcium, Reid Gap, Queensland. Natural size.

[Explanatory note continued on next page.]

In the dorsal valve there is a shallow, broad, median septum. The hinge-sockets receive the teeth in their deepest parts, and the serial sections suggest the presence of an accessory socket for the reception of a denticulum, as in more recent Terebratuloids (Muir-Wood, 1934, p. 518). Inner socket-ridges are well-defined, and are supported by the hinge-plates, which curve downwards and backwards towards the floor of the valve.

The cardinal process is very prominent, being about 2.5 cm. in length, and is bifid. The direction appears to vary somewhat in different specimens; in one sectioned specimen it is directed at right-angles to the plane of the commissure, in others it is directed more anteriorly. The base is much thickened by secondary shelly material and almost fills the space between the crural bases. The cardinal process branches into two wedge-shaped apophyses, which go towards the sides of the septum of the ventral valve, the flat edge of the wedge being parallel to the hinge-line.

Traces of the brachial loop may be seen in a few specimens, but unfortunately the material available is too poor for this structure to be properly studied.

The adductor muscle-scars are large and well separated, and there is a broad shallow median septum, which in the anterior region is bounded by thinner parts of the shell covering the vascular sinuses (Plate IV, fig. 1).

Remarks: The genus *Stringocephalus* Defrance resembles *Bornhardtina* Schulz externally, but *Bornhardtina* has no dorsal or ventral median septa and no large cardinal process (Ting, 1936). Three species of *Stringocephalus* from Europe and two species from China are recognised as valid by Cloud (1942). Of these, the Queensland specimens most closely resemble the genotype, *S. burtini*, and on the available evidence I can find no reason for distinguishing them from this European species.

Sub-family *Bornhardtininae* Cloud, 1942.

Genus *Bornhardtina* Schulz, 1914.

1914. Schulz, E., *Naturh. Voreins preuss. Rheinlande und Westphalens*, Verhandl., Jahrg. 70 (1913), pp. 363-366; Pl. 7, f. 6; Pl. 8, f. 1-3.

1936. Ting, T. H., *Geol. Soc. China, Bull.*, Vol. 15, No. 3, pp. 343-359.

1942. Cloud, P. E., *Geol. Soc. Amer. Special Paper No. 38*, pp. 100-104.

Genotype (designated Cloud, 1942): *Bornhardtina uncitoides* Schulz, 1914.

Diagnosis (after Cloud, p. 101): "Characteristically asymmetrical Stringocephalidae with deltidial plates conjunct at maturity, foramen hypothyriform, beak large and conspicuous, delthyrium occupying most of the posterior border.

"In the ventral valve the dental plates are obsolete and the muscle impressions relatively weak.

"In the dorsal valve the ventrally convex hinge plates are discrete and crural plates are absent. The thickening of the posterior border is ordinarily not pronounced but in some shells it is conspicuous. Full details of the loop structure are not known but such information as is available is consistent with the assignment to the Stringocephalidae."

Geological Range: Middle Devonian of Europe, generally coexistent with *Stringocephalus*.

[Continuation of explanatory note to Fig. 2.]

Distances of sections from the median vertical plane (in millimetres):

1=14.25, 2=13.30, 3=12.10, 4=11.60, 5=10.70, 6=9.75,
7=9.30, 8=8.15, 9=7.40, 10=6.85, 11=6.10, 12=5.30,
13=4.60, 14=4.30, 15=3.60, 16=3.15, 17=1.80, 18=0.0.

V=ventral valve, D=dorsal valve, a=interarea, s=septum, d=deltidial plate, f=foramen, t=tooth, hp=hinge plate, cp=cardinal process, cb=crural base.

***Bornhardtina coulteri* n.sp.**

Plate IV, fig. 7; Plate V, figs. 1-5.

Holotype: Sydney Univ. Coll. 7569. Loc. north-east corner of Por. 115, Par. Burdekin, 4 miles north of Attunga, N.S.W.

Horizon: 100 feet above the base of the Moore Creek Limestone, upper Middle Devonian (Givetian).

Diagnosis: Large, symmetrical *Bornhardtina*.

The black limestone contains abundant remains of shattered shells, but so far no complete specimen has been isolated from the rock. Plate V, fig. 1 shows the typical appearance of the rock. The specimen chosen as holotype is unfortunately incomplete, but the essential features are unmistakable. Nearly twenty specimens were sliced in attempting to work out the internal characters.

Exterior: The shells are large and globose, similar in shape to *Stringocephalus burtini*, the valves being usually symmetrical. Specimens, which I take to be immature shells, closely resemble the illustrations of the genoholotype (Schulz, 1914, Taf. VIII, figs. 1-3), and have a relatively high, erect beak in the ventral valve. These specimens show also very fine concentric and radiating ornamentation of the surface of the shell. In the larger, mature specimens the ventral beaks are very much incurved, and overhang the posterior portion of the dorsal valve (Plate V, fig. 5; text-fig. 3A). The dimensions of the shell are approximately as follows:

Height of ventral valve: 70 mm. Height of dorsal valve: 55 mm.

Width: 60 mm. Thickness: 55 mm. Distance between teeth: 30 mm.

The thickness of the shelly material in the region of the umbones is about 4 mm., but it is very much less than this in the anterior region, so that usually the lower part of the shell is crushed. The shell is fibrous and distinctly punctate. The cardinal margin is subterebratulid. Deltidial plates are large, apparently rather thin in some specimens, and form an outwardly concave surface (text-fig. 3B). The foramen is medially hypothryid, and a pedicle-collar is formed by the infolding of the deltidial plates around the former position of the peduncle. (See text-fig. 3B and Plate V, fig. 2.) This structure has been observed by Jackson (1916, p. 24), Thomson (1927, p. 75), Muir-Wood (1935, p. 521) and others in Mesozoic and Cainozoic Terebratulids, but does not seem to have been noticed hitherto in Palæozoic shells. Ventral palintropes are very narrow. Beak of the dorsal valve gently convex and almost covered by the ventral umbo. There is no trace of a fold or sulcus; anterior commissure probably rectimarginate.

In the ventral valve there is no trace of a septum and there are no dental plates. The teeth are typically terebratuloid and about 3 cm. apart; sections (cf. text-fig. 3A⁴) indicate the presence of denticula. The muscle scars are relatively large and vertically striated (Plate IV, fig. 7; Plate V, fig. 3).

In the dorsal valve there is no cardinal process, but there is a very small, concave area of muscle attachment immediately below the beak. The hinge plates are discrete and there are no crural plates. The crural bases are situated between the hinge plates, and support the delicate crura, which are about 3 mm. apart. Several specimens reveal crura as shown in text-fig. 3A, extending anteriorly and ventrally for about 1.5 cm., but the further extension of the loop is not known; a few specimens showed curved shelly plates lying within the valves, suggesting a structure comparable with the cross-plates of the loop of *Enantiosphen* (Cloud, 1942, Plate 26, fig. 6), but no organic connection with the valves could be proved. The muscle scars of the dorsal valve are not known.

Fig. A

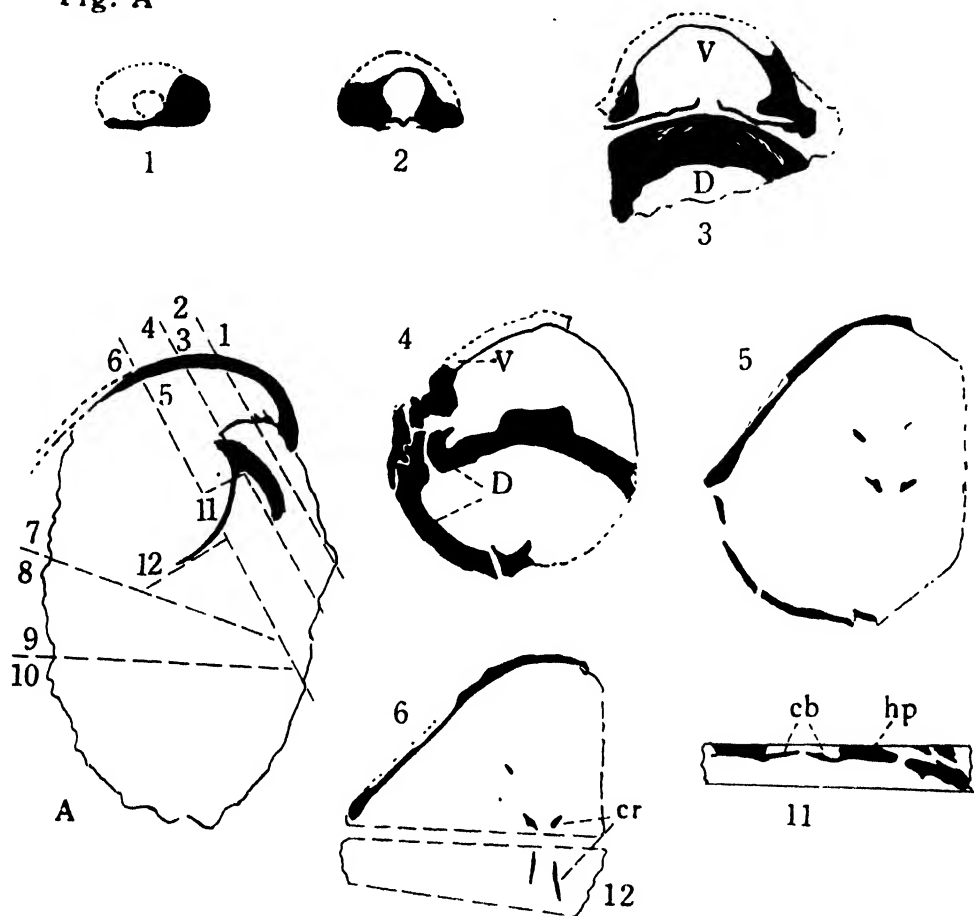


Fig. B

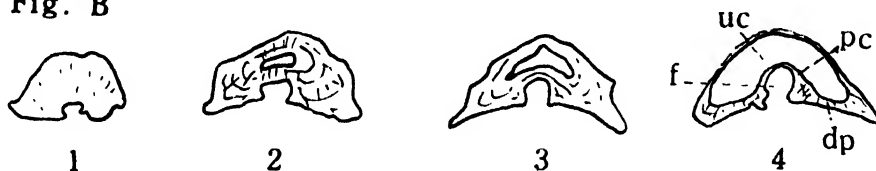


Fig. 3.—Sections through *Bornhardtina coulteri* n.sp. from limestone north of Sulcor, near Attunga, N.S.W. Natural size.

Fig. A.—Restored median vertical section showing beaks of ventral and dorsal valves, deltidial plate and crus. The specimen was sliced in the directions indicated 1-12. ($\times 1$.)

Figs. 1-6, 11, 12 illustrate the appearance along the corresponding directions indicated in Fig. A.

V=ventral valve, D=dorsal valve, hp=hinge-plate, cb=crural-base, cr=crura.

Fig. B.—Sections through the umbo of ventral valve, normal to the plane of symmetry. Distances from the tip of beak: 1=4.3 mm., 2=8.6 mm., 3=11.4 mm., 4=14.0 mm.

dp=deltoidal plate, f=foramen, pc=pedicle collar, uc=umbonal cavity. ($\times 1$.)

Remarks : *Bornhardtina* is distinguished from *Stringocephalus* by the absence of septa and a cardinal process. It appears to be related to *Rensselandia*, one or two species of which it may resemble in external shape, but the deltidial plates are conjunct and the form of the brachial support is distinctive. In *Rensselandia* the crura are short, divergent, and widely separated, and the loop follows the margin of the shell, whereas the crura of *Bornhardtina uncitoides* (figured Cloud, p. 103) are long, parallel and close together. The specimens under consideration thus appear to belong to the genus *Bornhardtina*. As already stated (p. 126) certain small specimens from Attunga resemble the outward form of the genotype, *B. uncitoides*, and it may be that this species is present, but, in the absence of comparative material, it seems preferable to erect a new species, *Bornhardtina coulteri*.

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EXPLANATION OF PLATES.

PLATE IV. Photo. I.A.B.

Figs. 1-3.—*Stringocephalus burtini* DeFrance. Queensland Univ. Coll. F.6977. Loc. Ryan's Quarry, Por. 62v, Par. Wyoming, Calcium, Reid Gap, Queensland. ($\times 1$.)

Fig. 1.—View showing pallial markings in dorsal valve, interarea, deltidial plates and foramen in ventral valve.

Fig. 2.—Side view showing both valves (internal mould).

Fig. 3.—View of ventral valve showing median septum.

Figs. 4-5.—Scale model of the umbonal region of dorsal valve of *Stringocephalus burtini* based on serial sections of specimen Queensland Univ. Coll. F.6976. ($\times 1$.)

Fig. 4.—Posterior view, showing large, bifid cardinal process and dental sockets.

Fig. 5.—Oblique lateral view, showing cardinal process, dental sockets, hinge plate and crural bases.

Fig. 6.—Median vertical section through *Stringocephalus burtini* specimen Queensland Univ. Coll. F.6976, showing foramen in ventral valve (6a) and cardinal process in dorsal valve (6b).

Fig. 7.—*Bornhardtina coulteri* n.sp. Sydney Univ. Coll. Loc. north-east part of Por. 115, Par. Burdekin, Attunga District, N.S.W., showing muscle scars in the ventral valve. ($\times 1$.)

PLATE V. Photo H. G. Gooch.

Bornhardtina coulteri n.sp.

All figured specimens are from north-east corner of Por. 115, Par. Burdekin, north of Attunga, New South Wales.

Fig. 1.—Slab of limestone showing typical preservation of shells. Specimen in upper right-hand corner shows trace of crus (cr.) below the beak of the dorsal valve. ($\times 1$ approx.)

Fig. 2.—Vertical section through beak of ventral valve, showing foramen (f.) and trace of pedicle-collar (p.c.).

Figs. 3-5.—*Bornhardtina coulteri* n.sp. Holotype. Syd. Univ. Coll. No. 7569. ($\times 1$ approx.)

Fig. 3.—View of ventral valve. Shelly material worn away from part of right-hand side, exposing impression of muscle scar.

Fig. 4.—Side view of same specimen, showing worn beak of ventral valve and section of dorsal valve.

Fig. 5.—Vertical median section of same specimen, showing overhanging beak of ventral valve, with trace of deltidial plate (d.p.) and dorsal valve with trace of descending crus (cr.). Note absence of cardinal process.

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PART IV

THE VIBRATIONS OF SQUARE MOLECULES.

PART I. THE NORMAL COORDINATES AND VIBRATION FREQUENCIES OF PLANAR AB₄ MOLECULES.

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INTRODUCTION.

One of the final stages in the assignment of a structure to a molecule is the calculation of the force constants of the normal vibrations in terms of the observed Raman and Infra-red frequencies. That these constants are invariable for molecules containing similar bonds has been shown by Glockler and Wall (1937), Crawford and Brinkley (1941) and others. Two procedures may be adopted. First the force constants may be taken from similar molecules and the frequencies of the given molecule calculated. Secondly, the force constants can be determined from the vibration frequencies, and since to a valence force approximation for symmetrical molecules there are usually more frequencies than force constants, relationships of self consistency can be examined. Agreement in either case provides a verification of the structure. In the case of unsymmetrical molecules the calculation of the frequencies may be very tedious, as an n-atomic molecule has $3n-6$ normal vibrations, whose frequencies are given as the roots of an algebraic equation of the $(3n-6)$ th degree. However, Wigner (1930) has shown how the theory of groups may be employed to factorise the secular equation in the case of symmetrical molecules.

In this case there are certain symmetry operations which transform the molecule into itself. These symmetry operations form a group. The kinetic (T) and potential (V) energies expressed in terms of the mass-reduced normal coordinates are

$$\begin{aligned} 2T &= \sum_{i=1}^{3n-6} \dot{Q}_i^2 \\ 2V &= \sum_{i=1}^{3n-6} \lambda_i Q_i^2 \end{aligned} \quad \dots\dots\dots (1)$$

where $\lambda_i = 4\pi^2\nu_i^2$, ν_i being the frequency. Since T and V are invariant under the operations of the group, a restriction is placed on the form of the normal coordinates. If R is an operation of the group, then

$$\left. \begin{aligned} RQ_i &= Q_i \text{ symmetric} \\ RQ_i &= -Q_i \text{ asymmetric} \end{aligned} \right\} \text{non-degenerate coordinate.} \quad \dots\dots\dots (2)$$

$$RQ_i = \sum_{j=1}^n R_{ij}Q_j \quad \text{degenerate coordinate.}$$

n is the degree of degeneracy, that is the number of vibrations having the same frequency.

Every group has a certain number of irreducible representations each of which represents a type of symmetry permitted to the normal coordinates. The latter will in general form a reducible representation of the group and by

reduction of this it is possible to determine the number of vibrations belonging to each symmetry type. The theory of groups can also be used to predict which of the irreducible representations of the symmetry group of the molecule will be active in the Raman or Infra-red spectrum. The depolarisation factor of the Raman lines can also be calculated. These considerations are of the utmost importance in correlating the observed frequencies with the normal vibrations.

Early work in this field was carried out by Duncan and Murray (1934), who investigated the normal vibrations of AB_4 molecules in connection with the Raman spectrum of nickel carbonyl, using Andrews' mechanical method (1930, 1934). Wilson (1935) has given the relationships between the frequencies and force constants to the valence force approximation, while Kohlrausch (1938) considered a more general model to the same approximation. Bernstein (1938) calculated the frequencies of the vibrations symmetrical to the fourfold axis. In connection with his investigation of the structure of inorganic complexes, Mathieu (1939) has described the normal vibrations of AB_4 molecules. However, no attempt has been made to determine the frequencies in terms of the force constants of the general potential function. Since six frequencies are obtainable from the Raman and Infra-red spectra of this type of molecule, the valence force model which uses only three constants is rather restrictive.

THE SYMMETRY COORDINATES.

Planar AB_4 molecules possess the symmetry D_{4h} . The classes of symmetry operations of the group D_{4h} are :

- (a) The identity operation E .
- (b) Twofold rotations around the fourfold axis C_2 .
- (c) Fourfold rotations around the fourfold axis C_4 .
- (d) Twofold rotations around the x and y axes C'_2 .
- (e) Twofold rotations around the diagonal axes C''_2 .
- (f) Inversion in the centre of symmetry I .
- (g) Fourfold rotations around the rotation-reflection axis S_4 .
- (h) Reflection in the xy plane σ_h .
- (i) Reflections in the xz and yz planes σ'_v .
- (j) Reflections in the diagonal planes σ''_v .

These symmetry elements are shown in Fig. 1.

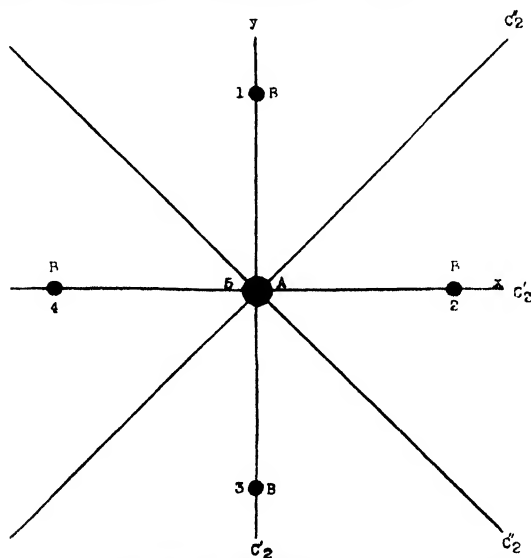


Fig. 1.—Coordinate axes of the AB_4 molecule.

Knowing the characters of the irreducible representations of D_{4h} and using the method of Wigner (*ibid.*), Wilson (1934) and Rosenthal and Murphy (1936), the reducible representation of the molecular vibrations can be expressed in terms of the irreducible representations of D_{4h} .

$$\Gamma = A_{1g} + A_{2u} + B_{1g} + B_{1u} + B_{2g} + 2E_u \dots\dots\dots (4)$$

In (4) A and B refer to symmetry and asymmetry of the irreducible representations with respect to C_4 , E represents a doubly degenerate irreducible representation, while g and u refer to symmetry and asymmetry with respect to inversion in the centre.

Sufficient information to determine the normal vibrations is given in Table I (cf. Wilson (1934a)). The symmetry type of each symmetry coordinate is set out together with the number of normal vibrations of that type and their properties with respect to the Raman and Infra-red spectra.

TABLE I.

Class.	No. of Vibs.	Coord.	Symmetry with respect to :										Active in		Polarisation.
			E.	C_2 .	C_4 .	C'_2 .	C''_2 .	I.	σ_h .	S_4 .	σ'_v .	σ''_v .	Raman.	I.R.	
A_{1g}	1	Q_1	+	+	+	+	+	+	+	+	+	+	Yes.	No.	P
A_{2u}	1	Q_2	+	+	+	-	-	-	-	-	+	+	No.	Yes.	—
B_{1g}	1	Q_3	+	+	-	-	+	+	+	-	-	+	Yes.	No.	D
B_{1u}	1	Q_4	+	+	-	-	+	-	-	+	+	-	No.	No.	—
B_{2g}	1	Q_5	+	+	-	+	-	+	+	-	+	-	Yes.	No.	D
E_u	2	S_{6a}, S_{7a} S_{6b}, S_{7b}	Transform like $x \pm iy$.										No.	Yes.	—

In Table I a +ve sign indicates that the symmetry coordinate considered transforms into itself under the given operation, while a -ve sign indicates that it transforms into its negative. The symmetry coordinates corresponding to the degenerate irreducible representation transform under the operations of the group like translations along the x and y axes.

It can be shown that the symmetry coordinates have the following properties :

$$(a) \quad 2T = \sum_{i=1}^{3n-6} \dot{S}_i^2$$

$$(b) \quad 2V = \sum_{i,j=1}^{3n-6} a_{ij} S_i S_j, \text{ with } a_{ij} = a_{ji} \dots\dots\dots (5)$$

a_{ij} is zero unless S_i and S_j belong to the same non-degenerate representation of the group or unless they transform identically under all the operations of the group in the case of a degenerate irreducible representation. From these considerations it can be shown that the secular equation is factored as follows :

(a) If there is only one symmetry coordinate belonging to a given non-degenerate irreducible representation, it will be given as the root of a linear equation and will be identical with the normal coordinate.

(b) If there are n symmetry coordinates belonging to a non-degenerate irreducible representation, then the frequencies will be given as the roots of an algebraic equation of the n th degree. The n normal coordinates will be given by linear combinations of the n symmetry coordinates.

(c) If there are n symmetry coordinates belonging to an m -fold degenerate irreducible representation, then the equation of the n th degree will be repeated m times.

So with the information shown in Table I five symmetry coordinates (Q_1 - Q_5) can be set up which are also normal coordinates and two sets S_{6a} , S_{7a} ; S_{6b} , S_{7b} , linear combinations of which give the corresponding normal coordinates. These are shown in Fig. 2.

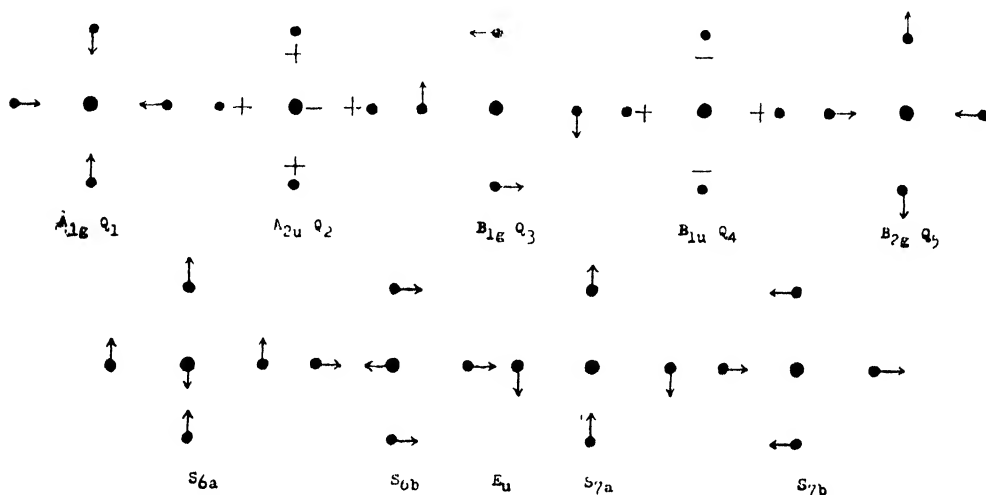


Fig. 2.—Vibrational symmetry coordinates of the AB_4 molecule.

KINETIC AND POTENTIAL ENERGIES AND VIBRATION FREQUENCIES.

The kinetic and potential energies in this system of coordinates can be obtained by the method of Wilson (1934b) also used by Silver and Shaffer (1941) in their study of planar AB_3 molecules. A set of cartesian axes with origin at the centre of gravity of the molecule and rotating with it, defined by the Eckart conditions (1935) is used. If m_i is the mass of the i th atom, the cartesian coordinates being x_i , y_i , z_i , the equilibrium values x_i^0 , y_i^0 , z_i^0 , and the displacements from the equilibrium values x'_i , y'_i , z'_i , then

$$x_i = x_i^0 + x'_i, \text{ etc.} \quad \dots\dots\dots (4)$$

The conditions are

$$\begin{aligned} \sum m_i \dot{x}'_i &= 0 \\ \sum m_i (x_i^0 \dot{y}'_i - y_i^0 \dot{x}'_i) &= 0 \quad \dots\dots\dots (5) \end{aligned}$$

together with the other four equations obtained by cyclic substitution.

In this coordinate system the internal kinetic energy of the molecule takes a very simple form

$$2T = \sum_{i=1}^5 m_i (\dot{x}'_i{}^2 + \dot{y}'_i{}^2 + \dot{z}'_i{}^2) \quad \dots\dots\dots (6)$$

which can be further simplified by the introduction of the mass-reduced coordinates

$$\xi_1 = m_1^{-1/2} x_1, \quad \eta_1 = m_1^{-1/2} y_1, \quad \zeta_1 = m_1^{-1/2} z_1 \quad \dots \dots \dots (7)$$

in terms of which

$$2T = \sum_{i=1}^5 (\dot{\xi}_i^2 + \dot{\eta}_i^2 + \dot{\zeta}_i^2) \quad \dots \dots \dots (8)$$

The coordinates representing the infinitesimal rigid translations and rotations of the molecule can be written down in terms of (ξ_1, η_1, ζ_1) . They are

$$Q_x = [m^{-1}(\xi_1 + \xi_2 + \xi_3 + \xi_4) + M^{-1}\xi_5] \quad \text{with } m_A = M, m_B = m \dots \dots (9)$$

with similar expressions for Q_y, Q_z . These represent translations along the x, y, z axis respectively. The coordinates representing rotation around the x, y, z axis are

$$\begin{aligned} Q\omega_x &= \zeta_1 - \zeta_3 \\ Q\omega_y &= \zeta_4 - \zeta_2 \\ Q\omega_z &= \xi_1 - \eta_2 - \xi_3 + \eta_4. \end{aligned} \quad \dots \dots \dots (10)$$

If $Q_x \dots Q\omega_z$ are each put equal to zero, the Eckart conditions are fulfilled. The symmetry coordinates can then be written down in terms of (ξ_1, η_1, ζ_1) , subject to two conditions:

- (a) That they are normalised to unity.
- (b) That they are orthogonal to the coordinates defined by (9, 10) and to themselves.

In this manner the following relationships are obtained:

$$\begin{aligned} Q_1 &= \frac{1}{2}(-\eta_1 - \xi_2 + \eta_3 + \xi_4) \\ Q_2 &= (2\sqrt{4m+M})^{-1} [M^{-1}(\zeta_1 + \zeta_2 + \zeta_3 + \zeta_4) - 4m^{-1}\zeta_5] \\ Q_3 &= \frac{1}{2}(-\xi_1 - \eta_2 + \xi_3 + \eta_4) \\ Q_4 &= \frac{1}{2}(-\zeta_1 + \zeta_2 - \zeta_3 + \zeta_4) \\ Q_5 &= \frac{1}{2}(\eta_1 - \xi_2 - \eta_3 + \xi_4) \quad \dots \dots \dots (11) \\ S_{6a} &= (2\sqrt{4m+M})^{-1} [M^{-1}(\eta_1 + \eta_2 + \eta_3 + \eta_4) - 4m^{-1}\eta_5] \\ S_{6b} &= (2\sqrt{4m+M})^{-1} [M^{-1}(\xi_1 + \xi_2 + \xi_3 + \xi_4) - 4m^{-1}\xi_5] \\ S_{7a} &= \frac{1}{2}(\eta_1 - \eta_1 + \eta_3 - \eta_4) \\ S_{7b} &= \frac{1}{2}(-\xi_1 + \xi_2 - \xi_3 + \xi_4) \end{aligned}$$

The symmetry coordinates form an orthonormal set, and so the inverse transformation is obtained by interchanging rows and columns in the matrix defined by (9, 10, 11). In this manner the following expressions are obtained:

$$\begin{aligned} \xi_5 &= -(\mu/M)^{1/2} S_{6b}, \quad \eta_5 = -(\mu/M)^{1/2} S_{6a}, \quad \zeta_5 = -(\mu/M)^{1/2} Q_2 \\ \xi_1 &= \frac{1}{2}(-Q_3 + \frac{1}{2}(\mu/m)^{1/2} S_{6b} - S_{7b}) \\ \eta_1 &= \frac{1}{2}(-Q_1 + Q_5 + \frac{1}{2}(\mu/m)^{1/2} S_{6a} + S_{7a}) \\ \zeta_1 &= \frac{1}{2}(\frac{1}{2}(\mu/m)^{1/2} Q_2 - Q_4) \\ \xi_2 &= \frac{1}{2}(-Q_1 - Q_5 + \frac{1}{2}(\mu/m)^{1/2} S_{6b} + S_{7b}) \\ \eta_2 &= \frac{1}{2}(-Q_3 + \frac{1}{2}(\mu/m)^{1/2} S_{6a} - S_{7a}) \\ \zeta_2 &= \frac{1}{2}(\frac{1}{2}(\mu/m)^{1/2} Q_2 + Q_4) \quad \dots \dots \dots (12) \\ \xi_3 &= \frac{1}{2}(Q_3 + \frac{1}{2}(\mu/m)^{1/2} S_{6b} - S_{7b}) \\ \eta_3 &= \frac{1}{2}(Q_1 - Q_5 + \frac{1}{2}(\mu/m)^{1/2} S_{6a} + S_{7a}) \\ \zeta_3 &= \frac{1}{2}(\frac{1}{2}(\mu/m)^{1/2} Q_2 - Q_4) \\ \xi_4 &= \frac{1}{2}(Q_1 + Q_5 + \frac{1}{2}(\mu/m)^{1/2} S_{6b} + S_{7b}) \\ \eta_4 &= \frac{1}{2}(Q_3 + \frac{1}{2}(\mu/m)^{1/2} S_{6a} - S_{7a}) \\ \zeta_4 &= \frac{1}{2}(\frac{1}{2}(\mu/m)^{1/2} Q_2 - Q_4) \end{aligned}$$

$$\text{with } \mu = \frac{4mM}{4m+M}$$

In terms of the symmetry coordinates it may be proved that the kinetic energy transforms into

$$2T = \sum_{i=1}^5 \dot{Q}_i^2 + \dot{S}_{6a}^2 + \dot{S}_{6b}^2 + \dot{S}_{7a}^2 + \dot{S}_{7b}^2 \quad \dots\dots\dots (13)$$

as may be verified by direct substitution in (8). The most general quadratic expression for the potential energy consistent with the symmetry is

$$2V = \sum_{i=1}^5 \frac{K_i}{\mu_i} Q_i^2 + \frac{K_6}{\mu} (S_{6a}^2 + S_{6b}^2) + \frac{K_7}{m} (S_{7a}^2 + S_{7b}^2) \quad \dots\dots\dots (14)$$

$$+ \frac{2K_{67}}{(m\mu)^{\frac{1}{2}}} (S_{6a}S_{7a} + S_{6b}S_{7b})$$

where $\mu_1 = \mu_3 = \mu_4 = \mu_5 = m$, $\mu_2 = \mu$.

Thus the solutions of the five linear factors are

$$v_i = \frac{1}{2\pi c} \left(\frac{K_i}{\mu_i} \right)^{\frac{1}{2}} \quad (i = 1 \dots 5) \quad \dots\dots\dots (15)$$

while the quadratic factors have the solution

$$v_{67} = \frac{1}{2\pi c} \left\{ \frac{K_6}{2\mu} + \frac{K_7}{2m} + \left[\left(\frac{K_6}{2\mu} - \frac{K_7}{2m} \right)^2 + \frac{K_{67}^2}{m\mu} \right]^{\frac{1}{2}} \right\}^{\frac{1}{2}} \quad \dots\dots\dots (16)$$

where ν is the frequency (cm^{-1}), c being the velocity of light.

THE POTENTIAL FUNCTION.

In setting up potential functions for molecules two approximations have been made, namely the valence force and the central force. In the first of these the forces are supposed to resist extension of the valence bonds and alterations of the valence angles. In the second case the forces are taken to act along the lines joining the nuclei. Thus in the non-linear AB_2 molecule the potential energies to the above approximations would be :

$$2V = k_r(\delta r_1^2 + \delta r_2^2) + k_\alpha(a\delta\alpha)^2 \quad \dots\dots\dots (17)$$

$$2V = k_r(\delta r_1^2 + \delta r_2^2) + k'_r\delta r_{12}^2 \quad \dots\dots\dots (18)$$

In (17) δr_1 and δr_2 are the changes in bond lengths, $\delta\alpha$ is the change in bond angle and a the bond distance, while in (18) δr_1 and δr_2 have the same meaning and δr_{12} is the change in distance between the two B atoms. In the case of a linear AB_2 molecule a change in $\delta\alpha$ from its equilibrium value of π does not alter δr_{12} to the required order of approximation, and so an additional term must be used to take account of the bending vibration. For this reason a valence force function modified by cross terms will be used in the following.

A general potential function consistent with the symmetry is given below :

$$2V = k_r \sum_{i=1}^4 (\delta r_i)^2 + 2k_{rr}(\delta r_1 + \delta r_3)(\delta r_2 + \delta r_4) + 2k'_{rr}(\delta r_1\delta r_3 + \delta r_2\delta r_4)$$

$$+ k_\alpha a^2 \sum_{i=1}^4 (\delta\alpha_i)^2 + 2k_{\alpha\alpha} a^2 (\delta\alpha_1 + \delta\alpha_3)(\delta\alpha_2 + \delta\alpha_4) + 2k'_{\alpha\alpha} a^2 (\delta\alpha_1\delta\alpha_3 + \delta\alpha_2\delta\alpha_4)$$

$$+ k_\beta a^2 \sum_{i=1}^4 (\delta\beta_i)^2 + 2k_{\beta\beta} a^2 (\delta\beta_1 + \delta\beta_3)(\delta\beta_2 + \delta\beta_4) + 2k'_{\beta\beta} a^2 (\delta\beta_1\delta\beta_3 + \delta\beta_2\delta\beta_4)$$

$$\dots\dots\dots (19)$$

$\delta\alpha_i$ is the angle in the plane between the displaced and equilibrium positions of the i th B atom. $\delta\beta_i$ is the similar angle for out of the plane displacements, while a is the A-B bond length. This is in conformity with Wilson's treatment but differs from that of Kohlrausch, who used

$$\delta\alpha_{ij} = \delta\alpha_i - \delta\alpha_j$$

for the "in the plane" vibrations. The above potential function reduces to Wilson's if

$$k_{rr} = k'_{rr} = k_{\alpha\alpha} = k'_{\alpha\alpha} = k_{\beta\beta} = k'_{\beta\beta} = 0.$$

δr_i , $\delta\alpha_i$, $\delta\beta_i$ can be expressed in terms of x_i , y_i , z_i ; then by the use of (12) in terms of the Q's and S's. The value of V thus obtained can be compared with (14) to yield the relationship (20) between the generalised constants K and the k 's.

$$\begin{aligned} K_1 &= k_r + 2k_{rr} + k'_{rr} \\ K_2 &= 4(k_\beta + 2k_{\beta\beta} + k'_{\beta\beta}) \\ K_3 &= k_\alpha - 2k_{\alpha\alpha} + k'_{\alpha\alpha} \\ K_4 &= k_r - 2k_{rr} + k'_{rr} \\ K_5 &= k_\beta - 2k_{\beta\beta} + k'_{\beta\beta} \dots\dots\dots (21) \\ K_6 &= 2(k_r - k'_{rr} + k_\alpha - k'_{\alpha\alpha}) \\ K_7 &= \frac{1}{2}(k_r - k'_{rr} + k_\alpha - k'_{\alpha\alpha}) \\ K_{67} &= k_r - k'_{rr} - k_\alpha + k'_{\alpha\alpha}. \end{aligned}$$

These values are then substituted in (15) and (16) to determine the frequencies. It is seen that the inclusion of the term k_{rr} removes the degeneracy between ν_1 and ν_4 inherent in the simple valence force treatment.

APPLICATION TO $[\text{Pt}(\text{CN})_4]^-$.

Physical and chemical evidence leads to the conclusion that the $[\text{Pt}(\text{CN})_4]^-$ ion is square. (For a review of the evidence see Mellor, 1942.) Mathieu (*ibid.*) has observed the Raman spectrum of this compound and observed the lines shown in Table 2.

TABLE 2.

Frequency (cm. ⁻¹) ..	95	318	455	465	2149	2168
Polarisation	D (?)	D	D	P	D	P
Assignment	ν_3	—	ν_4	ν_1	—	—

The treatment of this paper can be applied to $[\text{Pt}(\text{CN})_4]^-$ if it is assumed that the CN groups form approximately a dynamic unit. Since the CN stretching frequency is about 2,150 cm.⁻¹ this assumption should give a fair approximation. Wilson (1937, 1941) has shown that this treatment is justified where the ignored frequency is large compared with the others. As regards the assignment, 465 cm.⁻¹ must be the totally symmetrical vibration ν_1 . The depolarisation of 455 cm.⁻¹ would confirm its identification as ν_4 . 95 cm.⁻¹ could only be a deformation vibration and its depolarisation would suggest ν_3 . With this assignment the following values of k_r , k_{rr} , k_α can be obtained.

TABLE 3.

Constant.	$k \times 10^4$ dynes/cm.	
	This Paper.	Mathieu.
k_r	3.27	3.30
k_{rr}	0.036	—
k_α	0.139	—

It is seen that the value calculated by assuming the CN group rigid is in good agreement with Mathieu's value. k'_{rr} , $k_{\alpha\alpha}$, or $k'_{\alpha\alpha}$ and k_β would have to be obtained from a study of the Infra-red spectrum of this compound. Since only one "out of the plane" vibration is active, only k_β can be calculated.

The author wishes to thank Mr. D. P. Mellor for discussions on this topic and Mr. V. R. Stimson for checking the calculations.

SUMMARY.

Analytical expressions for the normal coordinates of the planar AB_4 molecule have been obtained, together with the relationships between the constants of the general potential function and those of a valence force potential function modified by the introduction of cross terms. The relationships derived are used to determine the stretching, bending and one interaction constant of the $[Pt(CN)_4]^-$ ion from its observed Raman spectrum.

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FURTHER DETERMINATIONS OF SPECIALISATION IN FLAX RUST CAUSED BY *MELAMPSORA LINI* (PERS.) LÉV.

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INTRODUCTION.

Investigations into the specialisation shown by *Melampsora Lini* (Pers.) LéV. in Australia were commenced in 1940 and the first results published in 1941 (Waterhouse and Watson, 2.). These showed the presence, in widely separated localities, of a physiological race unlike any previously recorded. Since then work has been continued along the same general lines, and by reason of the increasing importance of the crop and the damage the rust is doing, the later results are being frequently asked for and are therefore summarised herein for the period up to 31st December, 1942.

IDENTITY OF AUSTRALIAN RACES.

Using the set of differential varieties made available by Dr. H. H. Flor of North Dakota, six physiological races have been determined up to the present. These are designated here by letters in order to avoid confusion with numbers already given to described races: the allocation of the appropriate race numbers to them will be made at a later stage. At present a complication is introduced because the variety Argentine C.I. 705-1 behaves as an important addition to the standard varieties generally used.

The determinations are set out in the following table.

TABLE I.
Typical Reactions of Six Physiological Races of M. Lini on the Differential Varieties used in Specialisation Studies.

F. No.	Differential Variety.	C.I. No.	Reactions of Races.					
			A.	B.	C.	D.	E.	F.
1	Buda	270-1	R	S	S	S	S	S
2	Williston Golden	25-1	R	S	S	S	S	R
3	Akmolinsk	515-1	SR	S	S	S	S	SR
4	J.W.S.	708-1	I	S	S	S	S	I
5	Abyssinian	701	I	S	S	S	S	I
6	Kenya	709-1	I	SR	SR	S	S	I
7	Argentine	705-1	I	I	S	SR	S	I
8	Williston Brown	803-1	R	S	S	S	S	R
9	Very pale blue crimped	647-1	I	S	S	S	S	I
10	Ottawa 770B	355	I	I	I	I	I	I
11	Argentine	462	I	I	I	I	I	I
12	Bombay	42	S	I	I	I	I	S

The letters signify the following reactions: I, immune; R, resistant; SR, semi-resistant; S, susceptible.

Race A is the one already recorded for Australia (2.). It is essentially a rust of linseed varieties, and in these crops often does serious damage. It is not at present important on commercial fibre flax varieties, although it occurs in areas where these are grown. It occurs on *Linum marginale* Cunn. and is particularly virulent on Indian linseeds: varieties like Punjab, Bombay and Morocco are very heavily attacked by it.

Races B, C, D and E are serious pathogens on fibre flax varieties. They resemble rather closely Flor's (1940, 1.) race 21. Races B and C are similar except for a sharp differentiation made by Argentine 705-1; this gives immune and susceptible reactions respectively. Again, races D and E are paired. They differ from B and C in that Kenya 709-1 is fully susceptible to them, whilst it gives a variable or mixed reaction (recorded as "0; 2 and 3") to B and C. At high temperatures the reactions of D and E are of the variable type. As is the case with B and C, the separation between D and E is effected by the variety Argentine 705-1. Although a search has been made, no other variety has yet been found which will distinguish satisfactorily between races B, C, D and E. Our experience with Argentine 705-1 is in agreement with Flor's, namely, that it is a variety which is influenced by environmental conditions, and when inoculated with races B, C, D and E, has shown about 20% of mixing. In recording determinations with it, the predominant reaction has been used.

Race F shows affinities with race A, but is to be clearly separated from it by the reaction on Buda 270-1. It has been found so far only on *L. marginale* in Victoria and South Australia.

Contrasting the race determinations with those recorded for the U.S.A. races, it is notable that J.W.S. C.I. 708-1 is fully susceptible to races B, C, D and E. A striking feature of the six Australian races is that Ottawa 770B and Argentine C.I. 462 are uniformly immune.

GENETICS OF AUSTRALIAN RACES.

Preliminary work has shown that when two different isolates of teleutospores of race A were used, the æcidial stage developed on Punjab linseed gave reactions similar to those given by the original uredospore material, indicating that at least some isolates of this race are homozygous. More extensive tests are projected as well as crossing of the different races. Sporadic germination of the teleutospores has given a good deal of trouble in trying to work to plan.

The widespread natural infection of a perennial host like *L. marginale* makes it likely that natural crossing and the production of new races may not be uncommon.

DISTRIBUTION OF RACES.

Not only is it important to know what races occur, but also their distribution. In the following table is set out the distribution of the six races up to the end of last year.

TABLE II.

Distribution of the Six Races in Determinations up to 31st December, 1942.

Race.	Origin of Material.						Total.
	N.S.W.	Victoria.	South Australia.	Western Australia.	Tasmania.	N.Z.	
A	13	5	8	15	1	—	42
B	—	4	—	1	3	2	10
C	—	6	—	3	3	1	13
D	—	4	1	—	1	—	6
E	—	15	6	9	—	—	30
F	—	1	1	—	—	—	2
Totals ..	13	35	16	28	8	3	103

The presence of only race A in N.S.W. is explainable by the fact that only linseed varieties are grown here. If and when flax crops are grown, the rust flora may be expected to alter. Preliminary tests have shown that uredospores of race A are tolerant of considerably higher temperatures than those of the other four flax-attacking races and survive longer periods of artificial storage at low temperatures. In contrast with N.S.W., Victoria has yielded all six races.

From the breeder's point of view, the actual localities from which the races were derived is important. This information is as follows :

- Race A.* N.S.W. .. Leeton, Bourke, Macksville, Rooty Hill, Captain's Flat, Carroll, Gunnedah, Tichborne.
 S.A. .. Mount Gambier, Bangor, Gladstone, Coonawarra, Saddleworth, Paskeville.
 Vic. .. Jindwick, Riddell, Strathkellar, Koo-Wee-Rup, Wourn Ponds.
 W.A. .. Northam, Merredin, Beverley, Avondale, West Wagin, Boyup Brook, Woodman's Point.
 Tas. .. Chudleigh.
- Race B.* Vic. .. South Pakenham, Drouin, Woodglen, Riddell.
 W.A. .. Boyup Brook.
 Tas. .. Lilydale, Elizabeth Town.
 N.Z. .. Grove Town, Leeston.
- Race C.* Vic. .. Morwell, South Pakenham, Koo-Wee-Rup, Warnecourt.
 W.A. .. Roelands, Boyup Brook.
 Tas. .. Ulverstone, Smithton, Burnie.
 N.Z. .. Grove Town.
- Race D.* S.A. .. Goolwa.
 Vic. .. Ballarat, Maffra, Myrtleford, Winchelsea.
 Tas. .. Westbury.
- Race E.* S.A. .. Mount Gambier, Gladstone, Laura, Adelaide.
 Vic. .. Drouin, Myrtleford, Leongatha, Lake Bolac, Lindenow, Riddell, Strathkellar, Lismore, Warnecourt, Koo-Wee-Rup, Dalmare.
 W.A. .. Yarloop, Scott's Brook, Cookernup, Pinyarva, Rye Park, Mount Mumballup, Boyup Brook.
- Race F.* S.A. .. Wirrabara.
 Vic. .. Leongatha.

WILD FLAX IN RELATION TO RACE DISTRIBUTION.

Two wild flaxes are known in Australia. The widespread yellow-flowering weed, *L. gallicum* L., has not been found infected during the course of these studies, and attempts to infect it with races A, B, C, D and E have so far failed. The native *L. marginale* has been collected from the following localities, yielding the races as set down hereunder.

- Race A.* N.S.W. .. Bourke, Rooty Hill, Captain's Flat.
 S.A. .. Bangor (two collections).
 W.A. .. Woodman's Point, Wagin, West Wagin.
- Race E.* W.A. .. Scott's Brook.
- Race F.* Vic. .. Leongatha.
 S.A. .. Wirrabara.

There has been clear evidence of variation in *L. marginale* growing in different localities and of its being heterozygous in some instances. Distinct differences in the colour of the flowers have been noted.

Again, using a strain from N.Z. and inoculating it with race B, it was found that one plant in four was fully susceptible. This latter plant was grown to maturity. All its progeny were susceptible whilst the other plants gave resistant progeny. Similarly, when race D was used to inoculate plants of this N.Z. strain, one plant in three was fully susceptible, and in turn its progeny were all susceptible.

Material of *L. monogynum* Forst. s. from N.Z. gave infection results which may be summarised as follows :

	Race A.	Race B.	Race D.
Plants inoculated	32	5	3
Plants susceptible	21	4	2

It seems quite possible that certain strains of wild flax may serve as useful differentials of races.

BEHAVIOUR OF VARIETIES TESTED WITH KNOWN RACES.

Having sorted out the rust races, they have been used to determine the relative susceptibilities of numerous varieties of flax and linseed. Such a classification is essential from a breeding point of view. In certain varieties there is evidence of mixing ; in them the predominant reaction has been used.

The results are summarised in the following tables.

TABLE III.

Varieties of Flax and Linseed Resistant (Less than 10% of Plants Susceptible) to Races A, B, C, D, E and F.

F. No.	Variety.	C.I. No.	N.S.W. Dept. Agr. No.
10	Ottawa 770B	355	
11	Argentine Seln.	462	
19	Saginaw × Bombay	671	
48	Viking	981	
52	Rio	280	
55	Bison × 479	975	
61	Koto	842	
62	Russian × Argentine	896	
66	5126 B.37		
79	Uruguay		G 36/48
81	Seln. I.F. 22450/30		G 36/12
82	I.F. 812		G 38/7
97	Argentine	947	

TABLE IV.

*Varieties Resistant (Less than 10% of Plants Susceptible)
to Races B, C, D and E.*

F. No.	Variety.	C.I. No.	N.S.W. Dept. Agr. No.
10	Ottawa 770B	355	
11	Argentine Seln.	462	
12	Bombay	42	
14	Punjab		
19	Saginaw × Bombay	671	
48	Viking	981	
52	Rio	280	
55	Bison × 479	975	
61	Koto	842	
62	Russian × Argentine	896	
66	5126 B.37		
79	Uruguay		G 36/48
81	Seln. I.F. 22450/30		G 36/12
82	I.F. 812		G 38/7
97	Argentine	947	

TABLE V.

*Varieties Resistant (Less than 10% of Plants Susceptible)
to Races A and F.*

F. No.	Variety.	C.I. No.	N.S.W. Dept. Agr. No.
2	Williston Golden	25-1	
4	J.W.S.	708-1	
5	Abyssinian	701	
6	Kenya	709-1	
7	Argentine	705-1	
9	Very pale blue crimped	647-1	
10	Ottawa 770B	355	
11	Argentine Seln.	462	
16	Bolley's Golden	644	
17	do. Seln.	976	
18	Bison × Redwing	917	
19	Saginaw × Bombay	671	
21	Gossamer		
22	Stormont Cirrus		
48	Viking	981	
49	Redwing	320	
50	Bison × 649	984	
51	Bison × Redwing	916	
52	Rio	280	
53	Smoky Golden	1002	
55	Bison × 470	975	
56	Bison × Redwing	914	
57	Bison	389	
59	Bison × Redwing	970	
61	Koto	842	
62	Russian × Argentine	896	
64	Buda 80	1014	
65	Bison × Redwing	918	
66	5126 B.37		
67	Russian × Russian × Russian × Argentine	854	
68	Newland	188	
69	Bolley's Golden Seln.	977	
72	Gross Grain		G 36/47
73	Argentine		G 39/18
75	Zona Rosafe		G 39/27
76	Italian		G 38/15

TABLE V.—Continued.

*Varieties Resistant (Less than 10% of Plants Susceptible)
to Races A and F.—Continued.*

F. No.	Variety.	C.I. No.	N.S.W. Dept. Agr. No.
77	Uruguay		G 36/52
78	do.		G 36/49
79	do.		G 36/48
80	I.F. 808		G 38/11
81	I.F. 22450		G 36/12
82	I.F. 812		G 38/7
86	Walsh		Y 4681
87	Chippewa		
88	Rio		
89	Malabrigo		G 38/10
97	Argentine	947	
98	(Argentine 47 × Large Brown) × Smoky Golden ..		
102	Buda		Y 4673
103	Buda Seln.	737	
105	Cyprus		G 4883
106	Eikendorfer		G 36/44
108	H55 × A21-1		G 39/22
111	Linota		G 38/4
112	Moose × Seln. Y4674 ..		Y 4674
113	B. Moose × Redwing ..		Y 6202
114	do.		Y 6203
117	Moose × N. Dakota 127 ..		Y 6257
118	do.		Y 6259
119	do.		Y 6268
120	Moose × Bison		Y 6282
121	do.		Y 6282-1
122	do.		Y 6283
124	Moose × N. Dakota		Y 6284
125	Moose × Hybrid		Y 6288-1
126	Moose × N. Dakota		Y 6294
127	Moose × N. Dakota 127 ..		Y 6295-1
128	do.		Y 6295-2
129	Moose × Ottawa		Y 6299-1
130	do.		Y 6299-2
131	Moose × Redwing		Y 6304
133	Moose × Hybrid		Y 7688-2
134	Minnesota 11-29-1		G 39/34
135	Natural Hybrid 161	835	
136	Newland × (19 × 112) ..	839	
137	Punjab Seln.		SB 39/2
140	Pusa hybrid 50 × Aust. 2-1-1		G 39/9
141	Redwing C.A.N. 1		Y 2140
142	Reserve × (19 × 112)	739	
144	Selection 5872		G 38/9
145	T 11 × A 1-3		G 39/21-1
146	do.		G 39/21-3
147	do.		G 39/21-4
149	do.		G 39/21-7
150	Variety 420		G 37/3
158	Stormont Cirrus		
161	Blue Riga		
164	Recolite		
165	do.		
166	Minnesota II 29.1		
167	Minnesota II 30.52		
171	Beladi		
172	Hindi		
173	Giza Oil		
181	1150		

It will be seen that there are a number of varieties which are resistant to all six races. When grown in various localities, if they become rusted the indication will be that yet another race has turned up.

Without anticipating this needlessly, crossing work is well under way in which the aim is to combine the full resistance of certain of these parents with the other desirable characteristics of commercial flax and linseed varieties.

It is clear that the full resistance may also be obtained by crossing members of Table IV with those of Table V.

SUMMARY.

Determinations of rusted flax and linseed from Australia and New Zealand have shown that six physiological races occur. Four of these attack flax and show resemblances to each other and to Flor's U.S.A. race 21. The other two are markedly different and attack linseed varieties.

The distribution of the races throughout Australia is recorded.

Initial results of work on the genetics of one of these races indicate that it is homozygous.

The native flax, *L. marginale*, plays an important part as a perennial host of the rust. To date three of the races have been isolated from it in different States.

A classification of many varieties has been made on the basis of their relative resistance and susceptibility.

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A STUDY OF THE MAGNETIC BEHAVIOUR OF COMPLEXES CONTAINING THE PLATINUM METALS.

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Some years ago Van Vleck (1932) drew attention to the fact that complexes of the Pd and Pt transition series seemed, from the meagre data then available, to conform neither to the theory of free ions (with both spin and orbit contributing) so successful for compounds of the rare earths, nor to the Bose-Stoner "spin only"¹ theory which satisfactorily described the behaviour of many compounds of elements of the iron series. The incomplete 4*f* sub-shell responsible for the paramagnetism of the rare earths lies buried deep within the atom beyond the influence of interatomic forces and for this reason the rare earths stand in a class apart. It is therefore not surprising that there is no close resemblance between the magnetic behaviour of rare earth compounds and those of elements of the Pd and Pt transition series. On the other hand, the similarities of the electronic configurations of corresponding elements of the Fe, Pd and Pt series, in all of which the incomplete sub-shell (3*d*, 4*d* or 5*d*) responsible for paramagnetism lies outermost, might be expected to produce similar magnetic behaviour. The fact that the platinum metals do not conform to the "spin only" theory is no longer considered anomalous because this theory is not universally successful in accounting for the behaviour of even the iron transition series. For example, the compounds [Fe(dipy)₃]Cl₂ and K₂[Ni(CN)₄] are diamagnetic ($\mu=0$), whereas if the unmodified spin theory were applicable both compounds should be paramagnetic with susceptibilities corresponding to 5.9 and 2.8 Bohr magnetons respectively. It is obvious that, in addition to the quenching of orbital moment by asymmetrical electrostatic fields, other factors may come into play in determining the magnetic moment of an atom. A number of theories² have been developed to account for moments lower than those required by the "spin only" theory for ions (Pauling, 1931; Van Vleck, 1932, 1935). Pauling, for example, has accounted for the fall in moment in terms of the effect of covalent bond formation on the number of unpaired electron spins. Thus he discriminates between complexes in which atoms or groups of atoms are attached to a metal by ion dipole or electrostatic bonds (ionic complexes) as in [FeF₆]⁻ and [CoF₆]⁻ and those in which atoms or groups are attached by covalent bonds as in [Co(CN)₆]⁼ and [Fe(CN)₆]⁼ (covalent complexes). Owing to the pairing of electrons which takes place in the formation of a covalent bond there is a profound difference in the magnetic moments of Fe^{III} and Co^{III} in each of the two types of complexes. In the course of developing

¹ In the iron series the magnetic effect of orbital angular momentum is blotted out by the action of asymmetric electric fields of surrounding atoms with the result that the magnetic moment is given by the formula $\mu_s = \sqrt{S(S+1)}$, where *S*=the spin quantum number (Σs). A full discussion and the first satisfactory explanation of this quenching phenomenon has been given by Van Vleck (1932).

² Explanations alternative to Pauling's are (1) the crystalline potential theory of Penny and Schlapp, (2) Mulliken's theory of molecular orbitals. Van Vleck (1935) has demonstrated "the similarity of the predictions with all three theories".

his theory of the nature of the chemical bond Pauling predicted the magnetic moments of atoms of the Fe, Pd and Pt transition series as set out in Table I.

TABLE I.
Predicted Magnetic Moments of Complexes Containing Transition Elements.

The Iron Series.	The Palladium Series.	The Platinum Series.	No. of electrons in d shell (3d, 4d or 5d).	For ionic or sp ³ (tetrahedral) bonds.	For 4 dsp ² (square) bonds.	For 6 d ² sp ² (octahedral) bonds.
K ^I Ca ^{II} Sc ^{III} Ti ^{IV}	Rb ^I Sr ^{II} Y ^{III} Zr ^{IV} Nb ^V Mo ^{VI}	Cs ^I Ba ^{II} Hf ^{IV} Ta ^V W ^{VI}	0	0.00	0.00	0.00
V ^{IV}	Nb ^{IV} Mo ^V	W ^V	1	1.73	1.73	1.73
VIII ^{III} Cr ^{IV}	Mo ^{IV} Ru ^{VI}	W ^{IV} Os ^{VI}	2	2.83	2.83	2.83
VII ^{III} Cr ^{III} Mn ^{IV}	Mo ^{III}		3	3.88	3.88	3.88
Cr ^{II} Mn ^{III} Fe ^{IV}	Mo ^{II} Ru ^{IV}	Os ^{IV}	4	4.90	4.90	2.83
Mn ^{II} Fe ^{III} Co ^{IV}	Ru ^{III}	Os ^{III} Ir ^{IV}	5	5.91	3.88	1.73
Fe ^{II} Co ^{III}	Ru ^{II} Rh ^{III} Pd ^{IV}	Ir ^{III} Pt ^{IV}	6	4.90	2.83	0.00
Co ^{II} Ni ^{III}	Rh ^{II}	Ir ^{II}	7	3.88	1.73	
Ni ^{II}	Rh ^I Pd ^{II} Ag ^{III}	Pt ^{II} Au ^{III}	8	2.83	0.00	

This table is taken from the paper by L. Pauling and M. L. Huggins, *Zeit. für Kriol.*, 87, 1934, 214.

It will be seen that the moments (given in Bohr magnetons) depend on

- (1) The valence or oxidation state of the metal atom.
- (2) The nature of the bonds linking other atoms or groups to the metal (ionic or covalent).
- (3) The number and configuration of these bonds (when they happen to be covalent).

The iron series has been extensively examined in the light of Table I (Pauling, 1940) and from the experimental results it is clear that when allowance is made for small orbital contributions due to incomplete quenching in atoms not in S states, there is reasonably good agreement between theory and experiment for both ionic and covalent complexes.

It is a matter of some interest to enquire how far the predictions embodied in Table I hold good for the heavier and more complex atoms of the two later transition series. So far as the author is aware, no systematic study, such as is attempted here, has yet been made for the purpose of testing the extent of the validity of Pauling's predictions for the Pd and Pt series. It is true that a good many measurements on compounds of the platinum metals have already been reported but there are inadequacies in the data in the sense that a number of valence states have not received attention and a number of investigations have been largely confined to the sometimes poorly defined anhydrous chlorides whose magnetic dilution is low and whose identity and purity may be in doubt since analytical data were in these instances, not always reported.

From the experimental data already available, more especially that of Bose and Bhar (1928), Guthrie and Bourland (1931), Christiansen and Asmussen (1934, 1935), Janes (1935) and Cabrera and Duperier (1939) and the present work it is clear that the platinum metals do not form ionic complexes,³ a fact which is

³ It is possible that fluorides like RhF₃, PdF₃ and PdF₂, etc., may prove exceptions to this statement. The crystal structure of PdF₃ (Ebert, 1931) does indeed strongly suggest that Pd-F bonds are ionic. The author's attempts to prepare PdF₃ without the use of elementary fluorine were unsuccessful.

responsible for the diamagnetic or generally low paramagnetic susceptibilities of the compounds of these metals. Octahedral (d^2sp^3) complexes of Pt^{IV} , Pd^{IV} , Rh^{III} , Ru^{II} and Ir^{III} and square complexes of Pt^{II} and Pd^{II} are in point of fact all diamagnetic, which accords with Pauling's predictions for complexes of these types.

There are, however, instances where theory predicts paramagnetism as for example in the octahedral (d^2sp^3) complexes of Ru^{IV} , Os^{IV} , Ir^{IV} , Ru^{III} , Os^{III} , Ir^{II} , and Rh^{II} (see Table I). It is the purpose of the present communication to report results of measurements on complexes containing metal atoms in the above valence states. As far as practicable, attention has been centred on well defined, magnetically dilute compounds whose structure is known from either physical or chemical investigations.

EXPERIMENTAL.

Method of Measurement.

Susceptibilities were measured by the Gouy method, full details of which have already been given by Sugden (1932). The small tube used was calibrated for fields ranging up to 6,000 gauss by means of $CuSO_4 \cdot 5H_2O$ whose relatively small paramagnetic susceptibility was in the neighbourhood of the susceptibilities of the compounds studied. The following values of the specific susceptibility (χ) for $CuSO_4 \cdot 5H_2O$ have been reported :

$\chi \times 10^6$.	Temp. °C.	Author.
6.14	19.0	Sugden (1932).
5.82	19.2	Reekie (1939).
5.95	17.0	de Haas and Gorter (1930).
5.9	18.9	Feytis (1911).
5.85	18.9	Honda and Ishiwara (1915).

The average value corrected to 19° C. is 5.92×10^{-6} , and this was the value adopted for the present work. Effective magnetic moments were calculated on the assumption that the compounds, being magnetically dilute, obey Curie's Law: $\mu_{eff} = 2.839 \sqrt{\psi_M T}$. This assumption is undoubtedly only an approximation, but it is sufficiently close to the truth to test the validity of the predictions of Table I.⁴ All compounds were made from the purest starting materials available and analysed for at least one constituent to check their purity and to ensure their correct identification. Some identifications were also checked by means of X-ray powder photographs.

SUBSTANCES STUDIED.

COMPOUNDS OF RUTHENIUM.

Quadrivalent Ruthenium.

Potassium pentachlorohydroxyruthenate (IV) $K_2[RuCl_5OH]$. Relatively few compounds of quadrivalent ruthenium have been described, and of these two at least have been the subject of a good deal of investigation and not a little controversy. As a result of the work of Aoyama (1924), Howe (1904, 1927) and Charonnat (1931), the constitution of the brown and black complex chloro salts of ruthenium have been established as $K_2[RuCl_5OH]$ and $K_2[RuCl_6]$ respectively. Of the two, $K_2[RuCl_5OH]$ is the more easily prepared, and it forms a convenient starting material for the other chloro salts mentioned here. For the present work $K_2[RuCl_5OH]$ was made by the

⁴ It is possible that the deviations from Curie's law are considerable with the compounds $(NH_4)_2OsCl_6$ and $(NH_4)_2OsBr_6$. It is hoped to carry out low temperature measurements on these substances to check this point.

method of Antony and Lucchesi (1899) starting with the C.P. metal. The dark brown relatively insoluble crystals were analysed for chlorine; found Cl, 47.1%, 47.05%: calculated for $K_2[RuCl_5OH]$: Cl, 47.4%. As a rough check on the oxidation state of ruthenium in this compound, solutions were reduced with 0.0196N $SnCl_2$ (in excess) and then back titrated with standard iodine solution in the manner described by Howe (1927). For example, 25 ml. of $K_2[RuCl_5OH]$ solution required 3.4 ml. of 0.0196N $SnCl_2$ for its reduction to the trivalent state, whereas the amount required by theory was 3.5 ml. The reduction of $K_2[RuCl_5OH]$ with KI and $Ti_2(SO_4)_3$ has been studied by Crowell and Yost (1928) and there can be no doubt that in this compound the ruthenium is truly quadrivalent.

The valency of ruthenium in this compound is a matter of some interest in connection with later discussion of its magnetic behaviour which differs so radically from that of the closely related compound K_2RuCl_6 .

Potassium Hexachlororuthenate (IV) $K_2[RuCl_6]$. The starting material used for the preparation of this compound was the red chloro salt, $K_2[RuCl_5H_2O]$, formed as a result of the reduction of $K_2[RuCl_5OH]$ by prolonged boiling with alcohol under the conditions given by Charonnat (1931). The red chloro salt was dissolved in a minimum of 10N HCl and the solution saturated with chlorine. The hexachloro salt separated as fine, jet black cubes and octahedra which when crushed on white paper gave a deep wine red smear very similar to that produced by $K_2[IrCl_6]$. The compound was analysed for chlorine; found: Cl, 54.2%; calculated for $K_2[RuCl_6]$: Cl, 54.18%. The X-ray powder photograph of K_2RuCl_6 corresponded to a cubic lattice and was similar to the photographs produced by $K_2[IrCl_6]$ and $K_2[OsCl_6]$.

The hexachloro compound readily hydrolysed to the hydroxy compound, and several specimens of the hydroxy compound were prepared in this way. The extraordinary ease with which $K_2[RuCl_6]$ hydrolyses was noted by Charonnat, who states that even in 3N HCl the conversion to $K_2[RuCl_5OH]$ is almost complete.

Tervalent Ruthenium.

Potassium aquopentachlororuthenate (III) $K_2[RuCl_5H_2O]$. Since Ru^{III} complexes have already been extensively examined by Gleu and Cuntze (1938), one compound only was studied in the present work, and this mainly for the purpose of checking its constitution. $K_2[RuCl_5H_2O]$ was prepared following the method given by Charonnat (1931). When precipitated in a finely divided condition by means of alcohol, this substance possesses a light pinkish brown colour. The compound was analysed for chlorine; found: Cl, 47.3%. Calculated for $K_2[RuCl_5H_2O]$: Cl, 47.3%. The anhydrous compound $K_2[RuCl_5]$ was prepared by heating the aquo compound to a temperature of 300° C. in a stream of dry HCl. (Charonnat, 1931.)

RHODIUM COMPOUNDS.

Bivalent Rhodium.

As Rh^{III} complexes have been fully studied by Christiansen and Asmussen (1934), attention has been confined to Rh^{II} , the only other oxidation state in which well defined rhodium complexes appear to exist. Measurements were carried out on specimens described and analysed by Dwyer and Nyholm. They were as follows:

$RhCl_2SnCl_4(AsMePh_2)_3$. (Dwyer and Nyholm, 1942a.)

$Rh(AsMePh_2)_3Cl_2$. (Dwyer and Nyholm, 1941a.)

$Rh(AsMePh_2)_3Br_2$.

$[Rh(AsMe_2Ph)_4Br_2]$. (Dwyer and Nyholm, 1942b.)

$[RhPy_3Br]Br$.

$Py_6H_6[RhBr_4Py_2]$. (Dwyer and Nyholm, 1942c.)

The evidence for the state of oxidation of Rh in these complexes rests mainly on the analytical data but partly on their reducing action on silver nitrate solution. This reducing action was of course absent in the Rh^{III} analogues which have been described by Dwyer and Nyholm (1941b). From the analyses of numerous compounds there can be little doubt that, in the compounds under discussion, the Rh exists in the bivalent state. Work carried out recently in this laboratory on the polarography of Rh complexes clearly demonstrates the existence of Rh^{II} complexes at

the dropping mercury electrode.⁵ Although this work does not prove that such compounds can be easily isolated, it does show that they can be formed in solution by the action of moderately powerful reducing agents.

OSMIUM COMPOUNDS.

Sexavalent Osmium.

Potassium osmyloxynitrite trihydrate $K_2[OsO_3(NO_2)_2] \cdot 3H_2O$. This substance, first described by Wintrebert (1903) was prepared by the action of saturated KNO_3 solution on OsO_4 . The dark olive green needle-shaped crystals were analysed for nitrogen. Found: N, 6.2%; calculated for $K_2[OsO_3(NO_2)_2] \cdot 3H_2O$: N, 6.1%.

Quadrivalent Osmium.

Ammonium hexachloro-osmate (IV) $(NH_4)_2[OsCl_6]$. Among the most readily prepared and well defined compounds of Os^{IV} are the hexachloro and hexabromo salts, both of which have been deemed sufficiently stable for atomic weight determinations (Gilchrist, 1932). $(NH_4)_2[OsCl_6]$ and $(NH_4)_2[OsBr_6]$ were both prepared by Gilchrist's method, viz. digestion of OsO_4 with HCl (or HBr) and subsequent addition of NH_4Cl (or NH_4Br), except that recrystallization from weakly acid solutions was avoided owing to the possibility of hydrolysis to hydroxy compounds. Analyses: (I) Found: N, 6.4%, 6.5%; Os, 42.8%. Calculated for $(NH_4)_2OsCl_6$: N, 6.4%; Os, 43.3%. (II) Found: Os, 26.9%. Calculated for $(NH_4)_2[OsBr_6]$: Os, 26.95%.⁶ Osmium in each case was determined by igniting the salt in a stream of pure hydrogen. The identity of $(NH_4)_2[OsCl_6]$ was checked by means of an X-ray powder photograph. $K_2[OsCl_6]$ was prepared in a similar manner and also by treating $K_2[OsO_3(NO_2)_2]$ with concentrated HCl (Wintrebert, 1903). No analysis of the potassium salt was made.

Tervalent Osmium.

Potassium pentanitro-osmate (III) $K_2[Os(NO_2)_5]$. Attempts to prepare this salt by Wintrebert's (1903) method were not very successful owing mainly to the fact that $K_2[Os(NO_2)_5]$ was invariably accompanied by large amounts of $K_2[OsO_3(NO_2)_2] \cdot 3H_2O$. However, approximately 50 mg. of a substance corresponding to Wintrebert's description of the pentanitro complex were isolated. The amber yellow crystals were very soluble and quite stable in water. They were analysed for nitrogen. Found: N, 13.8%. Calculated for $K_2[Os(NO_2)_5]$: N, 14.0%. The pentanitro complex would seem to be the only⁷ stable Os^{III} complex so far described. Crowell, Brinton and Evenson (1938) studied $K_2[OsCl_6]$ in solution but succeeded in isolating only impure specimens of the solid.

Bivalent Osmium.

Potassium hexacyano-osmate (II) trihydrate $K_4[Os(CN)_6] \cdot 3H_2O$. This compound was prepared according to the method given by Krauss and Schrader (1928), viz. by the interaction of K_2OsO_4 and KCN. The colourless crystals (isomorphous with $K_4[Fe(CN)_6] \cdot 3H_2O$, Dufet, 1895) were analysed for nitrogen. Found: N, 15.2%. Calculated for $K_4[Os(CN)_6] \cdot 3H_2O$: N, 15.1%.

A NOTE ON THE ATOMIC WEIGHT OF OSMIUM.

There exists at the present a curious discrepancy between the atomic weight of Os as determined chemically by Gilchrist (1932) and that determined physically by Nier (1937). Although the former's value of 191.6 was accepted from 1935 to 1938, Nier's value of 190.2 is the one now adopted by the International Committee on Atomic Weights and the one used in the present work. In the past, when chemical and physical measurements have disagreed, subsequent chemical work has harmonized the values. (Cf. Be, B, Sb, etc., Aston, 1942.) This may well prove true with

⁵ Experiments carried out by J. B. Willis at the author's suggestion.

⁶ These analyses were made by Dr. G. Burger of the University of Adelaide.

⁷ A dipyridyl complex $[OsCl_2 \cdot 2dipy]Cl \cdot 3H_2O$ is mentioned by Burstall (1936), but no details have been published.

regard to osmium. There are remarkably close analogies between the chemistry of osmium and that of ruthenium (Wintrebert, 1903). As already mentioned, $K_2[RuCl_6]$ shows an extraordinary tendency to undergo hydrolysis to $K_2[RuCl_5OH]$ (Charonnat, 1931) which occurs even in 3N HCl. It seems very probable that Gilchrist's high value of 191.6 may be due to the contamination of the hexachloro (and hexabromo) salts with the corresponding hydroxy compounds, especially when it is recalled that the salts were purified by recrystallization from solutions containing as little as 7% HCl (or HBr). The author has noted subtle differences in the colour of various specimens of K_2OsCl_6 which did not seem to depend on the state of subdivision of the specimen but which may well have been due to the presence of the hydroxy salt, in amounts too small to be easily detected by analysis.

COMPOUNDS OF IRIDIUM.

Quadrivalent Iridium.

Ammonium hexachloro-iridate (IV) $(NH_4)_2[IrCl_6]$. Very few, if any, complex cations containing Ir^{IV} are reported in the literature; on the other hand complex anions are well known and easily prepared in the form of the hexachloro salts. The ammonium salt was prepared simply by adding NH_4Cl to H_2IrCl_6 , the latter having been prepared from iridium which had been purified according to hydrolytic method of Gilchrist (1932). Ammonium chloro-iridate (IV) crystallizes in jet black octahedra. Analysis for the metal was made by simply igniting the salt. Found: Ir, 43.77%. Calculated for $(NH_4)_2IrCl_6$: Ir, 43.70%. The identity of the salt was also checked by an X-ray powder photograph.

In preparing the potassium salt, the more direct method of passing chlorine over a heated mixture of Ir and KCl was employed. Since C.P. Ir and KCl were used for this preparation, no analysis of $K_2[IrCl_6]$ was made.

Bivalent Iridium.

From a search of the literature it would seem that with the possible exception of $IrCl_2$ (Wohler and Streicher, 1913), no compounds of bivalent iridium have been described. The very early work of Skobolikoff (1853) dealing with alleged Ir^{II} amines could not be confirmed by Palmaer (1895), who after a very extensive investigation stated that he was unable to prepare the amines of either Ir^{IV} or Ir^{II} . The complex measured $(Ir(AsMePh_2)_2Br_2)$ was prepared and described by Dwyer and Nyholm (1943). The results of the susceptibility measurements are set out in Tables IIA and IIR.

TABLE IIA.
Paramagnetic Compounds.

Compound.	Molecular Weight.	Specific Susceptibility. $\times 10^6$.	Temperature. ° K.	ψ_M .	Diamagnetic* Correction.	Atomic Susceptibility. ψ_A .	μ_{eff} Bohr Magnetons.	Number of Unpaired Electrons.
$(NH_4)_2[IrCl_6]$..	442	2.30	293	1,017	167	1,184	1.67	1
$K_2[IrCl_6]$..	484	2.02	295	978	171	1,149	1.65	1
$K_2[RuCl_6]$..	393	9.71	293	3,816	171	3,987	3.07	2
$K_2[OsCl_6]$..	481	1.47	294	707	171	878	1.44	—
$(NH_4)_2[OsCl_6]$..	489	1.63	290	716	167	883	1.44	—
$(NH_4)_2[OsBr_6]$..	706	1.01	291	713	238	951	1.49	—
$K_2[RuCl_5H_2O]^\dagger$..	375	4.31	293	1,616	160	1,776	2.04	1

* The diamagnetic corrections applied are those of Trew (1941), which are the means of the most reliable results in the literature.

† For $K_2[RuCl_5]$, $\mu = 1.8$ B.M.

TABLE IIB.
 Diamagnetic Compounds.

Compound.	Specific Susceptibility. $\chi \times 10^6$.	Compound.	Specific Susceptibility. $\chi \times 10^6$.
$K_2[RuCl_5OH]$	-0.49	$[RhPy_2Br]Br$	-0.31
$K_4[OS(CN)_4]3H_2O$	-0.10	$Py_2H_2[RhBr_2Py_2]$.. .	-0.12
$K_2[Os(NO)_2]^*$	-0.55	$[Rh(PhMe_2As)_2Br_2]$. .	-0.38
$[Rh(Ph_2MeAs)_2Br_2]_2$..	-0.4	$Ir(Ph_2MeAs)_2Br_2$.. .	-0.2
$[Rh(Ph_2MeAs)_2Cl_2]_2$. .	-0.5		

* I am indebted to Mr. W. A. Rawlinson of the Walter and Eliza Hall Institute of Research, Melbourne, for this measurement, which was made on 13.9 mgm. in water solution. The measurement was made by means of a Curie-Cheneveau Balance.

DISCUSSION.

COMPOUNDS WHICH CONFORM TO THEORY.

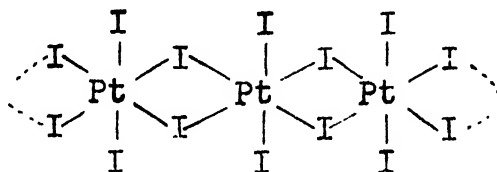
Diamagnetic Compounds.

It will be seen that Pauling's theory of magnetic moments accounts for the behaviour of a fairly wide range of platinum metal compounds, both para- and diamagnetic. Previous workers have shown that octahedral complexes of Pt^{IV} ,⁸ Pd^{IV} , Rh^{III} , Ir^{III} , Ru^{II} and square complexes of Pt^{II} and Pd^{II} are all diamagnetic, which is to be expected (see Table I). To this list must now be added octahedrally coordinated Os^{II} , whose complexes are also diamagnetic.

Paramagnetic Compounds.

Notwithstanding the fact that some paramagnetic platinum metal compounds have been previously reported and the fact that the present work adds several more to the list, compounds in this category form a minority group among the platinum metals. One of the most interesting cases brought to light is that of $K_2[RuCl_6]$, the effective moment (3.07 Bohr magnetons) of which shows that Ru^{IV} contains two unpaired electrons. This compound is notable as being the most strongly paramagnetic compound of the platinum metals described to date. Indeed so pronounced is its paramagnetism that the first preparation of the compound was mistakenly set aside as accidentally contaminated. On repeating the work there was no doubt about the high paramagnetic susceptibility which proved to be independent of field strength. To make sure that no accidental contamination had occurred, the $K_2[RuCl_6]$ was hydrolysed to $K_2[RuCl_5OH]$ and the susceptibility again measured. It was then found that the paramagnetism had entirely disappeared. Although this

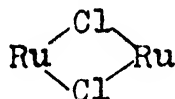
⁸ From Table I it appears that a substance like PtI_4 should have a moment of 4.9 Bohr magnetons, if the platinum is quadricovalent. Actually the substance is diamagnetic. (Unpublished work with J. B. Willis.) It is almost certain that the configuration of the platinum is not tetrahedral but octahedral:



If this is so, the diamagnetism of PtI_4 accords with Table I.

procedure proved beyond doubt that $K_2[RuCl_6]$ was not contaminated with any paramagnetic (or ferromagnetic) impurity, the diamagnetism of $K_2[RuCl_5OH]$ was a quite unexpected phenomenon.

Several compounds exhibited effective magnetic moments corresponding to the presence of one unpaired electron spin. To this class belong $K_2[IrCl_6]$ and $(NH_4)_2[IrCl_6]$, the moments for both of which correspond fairly closely to the theoretical value (1.73). In this respect the hexachloro-iridates are different from $K_2[RuCl_6]$, whose moment (3.07 Bohr magnetons) is somewhat greater than the theoretical value for two unpaired spins owing, no doubt, to some unquenched orbital contribution. This difference is interesting in view of the practically identical atomic environment of the iridium and ruthenium atoms in the potassium salts, a point which will be referred to again in the discussion of the hexachloro-osmates. One unpaired electron spin is found for Ru^{III} in $K_2[RuCl_5H_2O]$, although here again the moment (2.04 Bohr magnetons) is larger than the theoretical value owing to unquenched orbital contribution. The effective moment agrees reasonably well with that found by Gleu *et al.* (1936)⁹ for trivalent ruthenium ammines and also with the values reported by Malatesta (1938) and Guthrie and Bourland (1931) for other Ru^{III} complexes. The main interest of the present measurement is that it confirms the constitution proposed by Howe (1927) and Charonnat (1931) for the red chloro salt, viz. $K_2[RuCl_5H_2O]$. The moment of the anhydrous salt $K_2[RuCl_5]$ can be taken to mean that in preserving its coordination number of six, Ru^{III} does not form a Ru-Ru bond in this complex but instead forms a halogen bridge :



COMPOUNDS WHICH DO NOT CONFORM TO THEORY.

Paramagnetic Compounds.

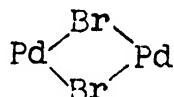
A moment in the neighbourhood of 2.8–3.0 Bohr magnetons was anticipated for $K_2[OsCl_6]$ and related compounds but the measured value is far short of this and is in fact even less than the value required for one unpaired electron spin. To determine the extent of the deviation from theory it is obvious that low temperature measurements are required for the hexachloro and hexabromosmates. One point is, however, worthy of comment. Since these osmium compounds form part of the isomorphous series $K_2[PtCl_6]$, $K_2[IrCl_6]$, $K_2[RuCl_6]$, etc., it would seem that departure from theory is not closely related to the effects produced by interatomic forces since, except for a small variation in the lattice constant, the environment of the platinum metal atoms is the same throughout the series.

Diamagnetic Compounds.

Among the elements of iron transition series, manganese has been examined in the widest range of oxidation states (from +2 to +7) and even in such a high oxidation state as +6 (in K_2MnO_4) conformity with Pauling's theory has been found (Goldenberg, 1940). It was therefore a matter of interest to see whether this was true of a heavy metal atom like osmium in a high oxidation state as in $K_2[OsO_3(NO_2)_2]$ for which μ should be in the neighbourhood of 2.83 Bohr magnetons. The observed value of zero would seem to show that Hund's rule requiring a maximum number of unpaired electrons (in the 5*d* sub-shell) breaks down for osmium.

⁹ The values given by Gleu and Rehm (1936) range from 2.00 to 2.07 Bohr magnetons.

Perhaps the most interesting complexes in this group are those in which the metal atoms should have an odd electron and a moment corresponding to one unpaired spin. Complexes of Rh^{II} and Ir^{II} fall into this group. A wide search was made for paramagnetic bivalent rhodium complexes, but entirely without success. The evidence for state of oxidation of Rh^{II} in the complexes studied has already been reviewed and there seems little doubt that one is here really dealing with Rh^{II} . In the polynuclear compounds there is the possibility that Rh-Rh bonds are formed by means of which the odd electron on each metal atom becomes paired as it does in Hg_2Cl_2 . X-ray crystal analysis (Wells, 1938) has shown that the bridge in the arsine complexes of palladium consists of two halogen (bromine) atoms :

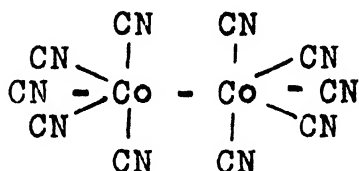


and in all probability the same kind of bridge functions in the Rh^{II} complexes. Since it is theoretically possible to formulate the binuclear Rh^{II} complexes in terms of Rh-Rh bonds, at the same time retaining octahedral coordination for the metal atom, efforts were made to secure compounds in which the possibility of metal to metal bonds was ruled out. Two such compounds, $[\text{RhPy}_5\text{Br}]\text{Br}$ and $[\text{Rh}(\text{AsMe}_2\text{Ph})_4\text{Br}_2]$, were examined and found to be diamagnetic.

It appears therefore that we have in the Rh^{II} complexes an instance of the quenching of spin moment, the mechanism of quenching being similar to that responsible for the disappearance of orbital moment in the transition elements other than the rare earths. A similar quenching of spin moment was observed in the one Ir^{II} compound measured. In regard to the quenching of spin, the electronic configuration of the two atoms (Rh^{II} and Ir^{II}) in d^2sp^3 complexes may possess some special significance ; in each instance the odd electron must occupy an outer unstable orbital (cf. Co^{II} ,¹⁰ Pauling, 1940) and in this situation it may be peculiarly liable to the quenching effect.

It is doubtful whether these are the only circumstances in which the electron spin is quenched because Os^{III} compounds¹¹ which should behave similarly to those of Ru^{III} and have moments in the neighbourhood of 1.73 Bohr magnetons are in point of fact diamagnetic ($\mu=0$). It must be admitted that the number of cases so far examined is very small owing to the fact that very few compounds of tervalent osmium have been described. One only, namely $\text{K}_2[\text{Os}(\text{NO}_2)_5]$, was studied in the present work and for this $\mu=0$, an observation in agreement

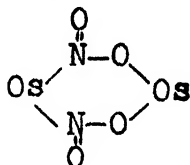
¹⁰ Unfortunately the data for Co^{II} are none too clear on this point ; $\text{K}_4[\text{Co}(\text{CN})_6]$ has been reported to be diamagnetic, but the substance is so unstable that its empirical composition cannot be regarded as established with any great certainty. There is evidence that in solution the cobaltocyanide ion has the composition $[\text{Co}(\text{CN})_5]^-$ (or $\text{Co}_2(\text{CN}_{10})$) (Glasstone and Speakman, 1930). The diamagnetism of the cobaltocyanide ion may be explained in terms of a structure such as :



This formulation finds some support from the measurements of Cambi and Ferrari (1935) on $\text{K}_4\text{Ca}[\text{Co}(\text{NO}_2)_6]$ and closely related compounds whose moments show that Co^{II} has one unpaired spin. On the other hand, if we accept the results of Cambi and Ferrari it must mean that there is no quenching of the spin of the electron occupying the unstable 4p orbital.

¹¹ The unpaired electron in Os^{III} and Ru^{III} occupies a stable orbital, viz. one of the 5d.

with Bose and Bhar's value of OsCl_3 .¹² With $\text{K}_2[\text{Os}(\text{NO}_2)_5]$ it is difficult to be sure whether we have a real departure from theory or not. The probability is that Os is not penta-coordinated here and that the complex is $[\text{Os}_2(\text{NO}_2)_{10}]$. In that event, there are two possible alternative structures, one involving a metal-metal bond, the other a bridge formed by two nitro groups:



That the nitro group can so bridge has been demonstrated by Mann and Purdie (1936), and it would seem that such a bridge is the more probable explanation of the structure of $\text{K}_2[\text{Os}(\text{NO}_2)_5]$. On the other hand, if the complex should contain the Os-Os bond its diamagnetism is not inconsistent with theory. Apart from crystal structure analysis there appears to be little prospect of distinguishing between these alternatives unless it can be shown that Os^{III} complexes which are definitely mononuclear have a moment of 1.73 Bohr magnetons.

One further curious anomaly remains to be noted, namely the difference between the magnetic moment of Ru^{IV} in $\text{K}_2[\text{RuCl}_6]$ ($\mu=3.07$ Bohr magnetons) and the moment of Ru^{IV} in $\text{K}_2[\text{RuCl}_5\text{OH}]$ ($\mu=0$). The quenching of the moment to be expected from two unpaired electron spins in the latter compound is extremely puzzling and the only circumstance of significance seems to be the difference in the symmetry of the crystalline field about the ruthenium atom in the two compounds. X-ray powder photographs of $\text{K}_2[\text{RuCl}_5\text{OH}]$ show that its symmetry is lower than cubic and it follows that there must be a correspondingly lower symmetry in the distribution of interatomic forces about the ruthenium atom; indeed the very nature of the complex ion itself suggests this. If this is the correct explanation of the phenomenon, it is not clear why the quenching of spin moment does not occur in $\text{K}_2[\text{RuCl}_5\text{H}_2\text{O}]$ ($\mu=2.04$ Bohr magnetons). Investigations of compounds of the type $[\text{Ir}^{\text{IV}}\text{A}_6]\text{X}_2$, $[\text{Rh}^{\text{IV}}\text{A}_6]\text{X}_2$ and $\text{K}_2[\text{IrX}_5\text{Y}]$ may throw more light on this question. There seems to be little doubt that covalent bond formation alone does not explain the abnormally low magnetism of complexes of the palladium and platinum metals since the moments found in certain instances are lower than those required by Pauling's theory.

In concluding his chapter on the palladium and platinum transition groups, Van Vleck (1932) wrote: "Further experimental data on the different salts of the Pd and Pt groups are greatly to be desired. Without them further discussion would be too speculative." The main purpose of this investigation has been to supply some of the previously missing data for the purpose of testing as far as possible the existing theories, with the hope that the discrepancies between theory and experiment which have been brought to light may lead to further theoretical investigation.

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The author is indebted to Messrs. F. P. Dwyer and R. S. Nyholm for their generous cooperation in making available compounds of rhodium and iridium; for their assistance in micro-analyses for chlorine and for the loan of ruthenium; to Mr. J. L. Sullivan for taking powder photographs of some of the materials used in this investigation; to Mrs. L. Buckley for micro-analyses for

¹² In discussing the moment of Os^{III} (in OsCl_3) Van Vleck (1932) has considered the possibility that strong internal magnetic coupling leading to quenching of both spin and orbital moment is responsible for the abnormally low magnetism, but he points out that a possibly insuperable objection to this explanation is the fact that Os^{III} is in a ^6S state.

nitrogen; and finally to the Commonwealth Research Fund for a grant to purchase osmium and iridium.

SUMMARY.

Complexes of the platinum metals in different valence states have been systematically examined with the object of testing the table of magnetic moments drawn up by Pauling for the transition elements. Over a wide range the predictions have been verified, but instances of breakdown have been observed, notably for Os^{VI} , Os^{IV} , Os^{III} , Ru^{IV} , Rh^{II} and Ir^{II} . Interesting examples of the quenching of spin moment have been noted among the complexes of Rh^{II} , Ir^{II} and Ru^{IV} .

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THE GEOLOGY OF THE COOMA DISTRICT, N.S.W.

PART II. THE COUNTRY BETWEEN BUNYAN AND COLINTON.

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With Plate VI.

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CONTENTS.

	Page
Introduction	156
Ordovician	157
Silurian	159
Cainozoic	161
(a) Basalt-flows	161
(b) Sediments	164
Igneous Intrusions.. .. .	164
(A) The Cooma Gneiss	164
(B) The Murrumbidgee Batholith	165
(C) Porphyries and Porphyrites	167
(a) Granite-porphyries	167
(b) Other Porphyries and Porphyrites	168
(D) Genetic Relations among the Igneous Rocks	169
(E) Quartz-Dolerites	169
Geological Structure of the Palæozoic Rocks	170
Structural Relations of Ordovician and Silurian Rocks	171
Summary	172
References	172

INTRODUCTION.

Nearly thirty years ago an account was given of the geology of the country around Cooma (Browne, 1914); this was to have been followed by detailed petrological studies, but it was considered desirable first to map the country to the north, and the field-survey on which the present paper is based was begun as far back as 1917. Various circumstances interfered with the completion of the work, though references to some aspects of it were included in other papers (Browne, 1929, 1931*a*, 1933). Detailed field- and laboratory-studies of the petrology of the metamorphic rocks of the Cooma area have since been undertaken by Dr. Germaine A. Joplin, who has already published two valuable papers on the subject (Joplin, 1939 and 1942).

The field-work was made possible by the unbounded kindness and hospitality of many local residents, including the late Mr. T. J. Sherlock and family of "Kiaora" near Cooma, the late Mr. and Mrs. V. Fraser of Murrumbucka, Mr. and Mrs. J. J. Harnett, formerly of "Gurrabeal", Mr. and Mrs. H. Fane de Salis, late of Chakola, the late Mrs. Cosgrove of "Oakvale", and the late Mr. A. Cosgrove and Mrs. Cosgrove of Billilingra House.

I am much indebted to Dr. Joplin for drawing the maps, for the loan of microslides and for discussion.

The area mapped and investigated extends to the Colinton Gorge, some 30 miles north of Cooma. For the most part only the field-relations and megascopic characters of the rocks have been studied, but in some instances microslides have been examined. The investigation has served to confirm some of the conclusions and interpretations put forward in the 1914 paper and has proved others to be in error. Reference will be made to these in the appropriate places.

The principal formations whose northerly extensions have been studied are :

- (1) An Upper Ordovician series, chiefly of sediments, metamorphosed to varying degrees ;
- (2) An Upper Silurian series, also mainly sedimentary ;
- (3) A late Ordovician or epi-Ordovician intrusion, known as the Cooma gneiss, intimately penetrating the most altered parts of (1) ;
- (4) A late Silurian intrusion with a considerable extension to the north, which may be called the Murrumbidgee bathylith. Its component rocks are gneissic—the blue, white and pink gneisses of the earlier paper ;
- (5) Granite-porphyrries, thought to be of late Silurian age ;
- (6) Porphyries, felsites and porphyrites mostly of post-Silurian age.

In addition to these there are minor dolerite intrusions of unknown age, Tertiary basalt-flows and dykes and Tertiary and post-Tertiary gravels and other alluvium.

The area examined is roughly divisible both geologically and physiographically into two parts. In general the Silurian and less altered Ordovician rocks form relatively low, undulating country, most of which lies to the east of the Murrumbidgee ; west of the river the Ordovician schists and granites and the late Silurian gneiss, which are more resistant to erosion, rise in the south to heights of more than 3,000, and farther north to 4,400 feet above the sea, forming country in places rugged and deeply dissected. A distinct relation can be observed between geology and physiography not only in the broad way but often also in matters of detail.

ORDOVICIAN.

In the 1914 paper it was pointed out that west of Cooma a gradual eastward transition could be traced from graptolite-bearing Ordovician slates through phyllites and schists into rocks granitized by the Cooma gneiss. In 1931 on Cottage Creek, some 15 miles south of Cooma, graptolites, including *Diplograptus bicornis*, were found in black and grey shales or slates on the strike of the schists (Browne, 1931b) ; this discovery suggested that the latter were of Upper Ordovician age,* and showed that their metamorphism was not continued along the strike but was in all probability peripheral to the Cooma gneiss. Dr. Joplin has divided the Ordovician sequence west of Cooma into the Coolringdon beds, chiefly of siliceous slates, and the Binjura beds lying to the east of them, and composed of alternating shaly and sandy beds now metamorphosed. She has also demonstrated conclusively the causal relation existing between the Cooma gneiss and the metamorphism, and has been able to plot zones of progressive alteration marked by the entry of certain index-minerals.

* The statement in the 1914 paper that *Didymograptus* and *Tetragraptus* were associated with *Diplograptus* at Geygedzerick Hill near Berridale was an unfortunate and unaccountable error.

The northern extensions of these zones have been traced by Dr. Joplin and are described by her in a paper shortly to be published in the *Proceedings of the Linnean Society of New South Wales*.

The rocks of most of the zones are easily identifiable in the field ; for example the blue-black slates cropping out near McCarthy's Crossing, 7 miles north-west of Cooma, may be observed again near the mouth of Bulga Creek, 4 miles to the north, and have been noted at the head of Long Creek outside the limits of the map. The belt of andalusite-schist (Slack's Creek phyllites) passes to the west of Muddah Lake, reappears from beneath Tertiary basalt in the headwaters of Barkgunyah Creek, and has been picked up again in Long Creek about two miles up from "Oakvale", north of which it is cut off by the Murrumbidgee bathylith.

Good exposures of the schists of the Binjura beds may be seen in the western tributaries of Pilot Creek and along Barkgunyah and Long Creeks. The beds are more or less granitized, and include two rather distinctive types. One of these, which for field-purposes has been designated the *corduroy granulite*, is really a fine-textured paragneiss in which bands of light-coloured material, about one-tenth of an inch wide, alternate with still narrower layers rich in biotite ; the other, the mottled gneiss, was originally thought from its transgressive relations to be a much contaminated igneous type, but Dr. Joplin has shown that it is a granitized sedimentary schist. Its position has been noted on the map only where it has been encountered in the course of the survey.

Along the ridge which runs from Mittagang Bridge to Murrumbucka Gap on the left bank of the Murrumbidgee the granitized rocks make prominent outcrops, flanked east and west by bars of Cooma gneiss and the blue gneiss of the Murrumbidgee bathylith. Further north inclusions of the granitized rocks are seen at intervals in the blue gneiss, especially in its eastern half, as in Sandy and Spring Vale Creeks, at the head of Colinton Gorge, and elsewhere. The mottled gneiss has not been observed north of Sandy Creek. Good sections showing intimate penetration of granulites by Cooma gneiss are to be seen along the Murrumbidgee above and below Mittagang Bridge.

In the zones of higher grade metamorphism only slight indications of contemporaneous Ordovician igneous activity are visible. Dr. Joplin (1942) has shown that in Cooma certain granulites containing hornblende and sometimes pyroxene, which are enclosed in the Cooma gneiss, are basic in composition and probably represent former basalt-flows or dolerite-sills. Further north lenses of similar rocks are to be seen at several points enclosed in the blue gneiss, mostly at less than three-quarters of a mile from its eastern margin. Along the road from Cooma to Mittagang two miles past the cemetery such inclusions were formerly to be seen, intimately penetrated by blue gneiss, and several have been noted in the parishes of York and Bullanamang near "Dromore" and "Riversdale" homesteads, in Sandy Creek, and in Spring Vale and Long Flat Creeks. Some of the rocks have been completely recrystallized but others retain relics of former minerals and structures. Grainsize is very variable and may be quite coarse, and field-evidence is not lacking of interaction between host and inclusion. It is, of course, possible that some of these amphibole-rocks are intrusions comagmatic with though antecedent to the blue gneiss, and therefore of Silurian age.

The Ordovician rocks lying to the east of the Murrumbidgee bathylith offer a most remarkable contrast to those just described, both in composition and in grade of metamorphism. The black slates and chloritic phyllites cropping out at Bunyan and to the south of it continue to the north but with decreasing importance, being apparently encroached upon gradually by the blue gneiss. The most abundant rock-types are schistose acid crystal-tuffs and schistose rhyolites. Rocks of these types can be traced from Bushy Hill east of Cooma at intervals to Bunyan and through the parish of Woolmulla, but attain greater

extent and importance in the parish of Callaghan, and form the bulk of the Ordovician rocks in Billilngra and Bransby. The degree of crushing and recrystallization may be such as to obliterate all traces of the original rocks, but the alteration is always of low grade. Just south of the Colinton gorge there seems to be an almost unsheared core of the rhyolite grading outwards into the sheared or crushed phase. Other sheared rocks appear to have been felspathic grits, and the coarsest type, found in the parish of Callaghan, is a quartz-grit which becomes conglomeratic, with pebbles up to $1\frac{1}{2}$ inches in length.

A little limestone is seen, always in small lenses, always recrystallized, and with no traces of fossils. The most southerly, overlooked in the 1914 survey, is on the railway line $3\frac{1}{2}$ miles north of Cooma; this is in part silicified and silicated by a tongue of acid blue gneiss. Another small patch is on the roadside at Pearman's Hill and three others have been noted in the parish of Bransby at or near the Ordovician-Silurian boundary.

A very constant feature of the Ordovician *terrain* is a series of sill-like intrusions of schistose quartz-porphry or porphyroid. Though recognized at Bushy Hill and south of Bunyan, it becomes conspicuous first in the parish of Woolumla, where its dark green colour contrasts with that of the schistose rhyolites and tuffs. It makes strong outcrops on the right bank of the Murrumbidgee near its junction with the Bredbo, and further north in the parishes of Bullanamang and Bransby, where it is in contact with the blue gneiss. Particularly good sections may be studied up Spring Vale Creek, and in the Colinton gorge, where the Ordovician belt has narrowed considerably and about two-thirds of its width is of porphyroid dipping to the west, the remainder being schistose rhyolite, of which also many lenses are enclosed in the intrusive rock.

The porphyroid is essentially a product of low-grade metamorphism; chlorite and sericite are abundant in it and crushing and straining of the quartz phenocrysts are characteristic. The rock is in places banded parallel to the planes of schistosity, which are remarkably even and regular and appear to conform with the boundaries of the associated phyllites and slates. The geological age of these porphyroids is not known with certainty, but in their degree of alteration they are more closely allied to the Ordovician than to the Silurian rocks described below, and provisionally they are assigned a late Ordovician age.

The proximity of the slates, phyllites, porphyroids and other low-grade rocks of the eastern belt to the Cooma gneiss and granitized schists is a matter that calls for comment. Owing to the interposition of blue gneiss, nowhere can a gradation be traced between them, but in places less than half a mile separates their outcrops, and near the entrance to Colinton gorge lenses of porphyroid enclosed in the blue gneiss are very close to and on the same strike as inclusions of granitized schist and Cooma gneiss. It may be, of course, that, as suggested in the 1914 paper, the metamorphic effect of the Cooma gneiss was much greater on the west than on the east, due to the shape of the mass and the attitude of the enclosing rocks, and perhaps also to the fact that pressure during crystallization came from the east. It may be also that the inclusions in the blue gneiss changed their relative positions as the result of compression during the crystallization of the latter. Nevertheless the possibility of overthrusting having occurred and brought high- and low-grade rocks into apposition before the intrusion of the blue gneiss, though incapable of proof, cannot be lightly dismissed.

SILURIAN.

The Silurian rocks were not mapped or studied for any great distance from their western boundary. They lie entirely to the east of the Ordovician belt with a submeridional strike and variable dips. Clay-slates imperfectly cleaved and in places differing but little from shales are perhaps the dominant rocks, especially near the Ordovician boundary. Massive and flaggy sandstone and

quartzite appear with them west of and along the railway in the parish of Callaghan. Undoubtedly, however, the most interesting rock-types are the acid crystal-tuffs which form an important proportion of the sediments. These are characterized by abundant grains of quartz and felspar, generally with hornblende and biotite and a variable proportion of cryptocrystalline matrix. Angular rock-fragments up to a few inches in length may be locally abundant, and in Por. 22, Par. Billilingra rounded pebbles of quartz-porphry convert the rock into a tuffaceous conglomerate. Alteration of the constituent minerals to albite, chlorite, epidote, etc., is common and the rocks often show jointing and other signs of strain.

The distribution of the tuffs is rather capricious, the belts being somewhat discontinuous, and for many of the exposures accurate mapping is difficult or impossible. The behaviour of the rocks is rather like that of intrusives, outcrops making and ceasing abruptly, or tapering out and transgressing the strike of the associated slates. Elsewhere they are distinctly bedded and show gradations and variations in grain-size like ordinary clastic sediments. Some of the rocks, plentifully studded with grains of quartz and felspar, are clearly recognizable in hand-specimen as fragmental, but others, in which the matrix is more prominent, have the appearance of porphyries. Moreover the tuffs themselves may be intimately invaded by quartz-porphry, and it is almost or quite impossible to distinguish between the two types in hand-specimen and sometimes even in thin section. Not improbably some of the doubtful types are really porphyries which have picked up mineral fragments on their way through the tuffs.

Good sections of these rocks are few, but on the railway-line between 2 and 3 miles north of Bredbo two low cuttings afford opportunities to study their characters and their relations to the slates. In these the suggestion of intrusion is produced by marginal hardening of the associated slates, by inclusions of hardened, cherty shale in the tuff and by long tongues of tuff transgressing the slate. The tuffs also enclose ellipsoids of recrystallized limestone in some of which fossil corals and brachiopods may be observed, recalling the somewhat similar occurrences at Yass and Jenolan.

In the 1914 paper the tuffaceous character of these rocks was not fully recognized, largely owing to their close association in the field with true igneous rocks, and they were all grouped as porphyries.

The tuffs attain probably their greatest development in the parish of Bransby (Fig. 1). Two or three miles north of Bredbo they extend from the railway line east to the road and beyond it for at least another three-quarters of a mile.

In the parish of Callaghan (Fig. 2) tuffs exactly similar to those just described are found among the Ordovician beds not far from the Silurian boundary. Though marginally somewhat sheared, the outcrops are in the main perfectly massive and in marked contrast to the highly schistose rocks around them. Similar rocks appear in Por. 48, Par. Billilingra and elsewhere. The occurrence of these tuffs among the older rocks heightens the impression that they are intrusive, but does nothing to elucidate the mystery of their emplacement.

A little impure fossiliferous limestone crops out in Gungoandra Creek a mile south of the Colinton gorge and some has been observed in the ridge north of Bredbo outside the limits of the map. Apart from the crystal-tuffs contemporaneous volcanic activity is indicated by a basic lava-flow, much carbonated and possibly spilitic, on a ridge in Por. 96, Par. Bransby, and by a well-banded felsitic rhyolite, possibly 150 feet thick and three-quarters of a mile long, in Pors. 23 and 41, Par. Billilingra. A smaller outcrop of fluidal rhyolite at the very base of the Silurian beds in the north-east corner of Por. 24 of the same parish is also probably a flow.

It seems possible that only the western parts of the Silurian sequence are characterized by the presence of igneous material. A reconnaissance trip along the road for 20 miles from Cooma in a north-east direction to Umaralla and beyond revealed that east of Rock Flat Creek there are only shales, slates, quartzites and impure limestones.

Fossils have been found at various points. The shales at Billilingra Siding have yielded *Encrinurus mitchelli* Eth. fil., Brachiopoda indet., *Alveolites* sp., *Favosites* sp., *Heliolites* sp., (?) *Hercophyllum* sp. An impure limestone in Gungoandra Creek one mile south of Colinton gorge contained *Hercophyllum shearsbyi* (Sussmilch), "*Cystiphyllum*" sp., *Mucophyllum crateriodes* Eth. fil., and *Favosites allani* Jones. *Favosites* and a small Orthid have been got from limestone ellipsoids in tuff in a railway cutting $2\frac{1}{2}$ miles north of Bredbo. These fossils, for whose identification I am indebted to Dr. Ida A. Brown, all came from approximately the same horizon and indicate a correlation with the lower part of the Upper Silurian Hume Series of the Yass district. It is very probable that more careful collecting would enable closer and more detailed correlations with the type-area at Yass and help in the elucidation of the geological structure.

CAINOZOIC.

(a) *Basalt-Flows.*

These crop out extensively in the parish of Murrumbucka. Remnants of basalt are seen at about 20 feet above the river near Mittagang Bridge, and more extensive relics are found on the sides and floor of the valley of Pilot Creek. Three or four miles up this creek the basalt rises abruptly from the valley through about 400 feet to form a flat-topped plateau area which extends north for a couple of miles and then westward almost to the Murrumbidgee. Along the track from Muddah Lake south to McCarthy's Crossing further thin patches of basalt are encountered on the plateau surface. A westward view from Reeve's Point, one of these remnants, itself some 600 feet above the river, makes it clear that the basalt crops out extensively in the river valley, and there are evidences that it once filled the valley at a time when its floor was 20 or 30 feet above its present level.

In the eastern part of the area examined basalt is almost entirely lacking. A couple of small patches survive in the parish of Woolumla within a radius of a mile from Chakola railway station. It is hard to understand why these should have escaped erosion, for neither is favourably situated for preservation.

The basalt of the flows is the usual olivine-bearing type with augite that appears slightly titaniferous. Physiographic considerations suggest that the flows are of Pliocene age for they occupy parts of the broad lowland area eroded by the Murrumbidgee system out of the Miocene surface forming the plateau. It is evident that they filled river valleys to a depth of at least 600 feet and spread over the higher ground, smoothing out its inequalities. A succession of flows is indicated by terracing or trap-featuring, and there has evidently been considerable erosion since the eruptions.

A former extension of the basalt to Pearman's Hill is inferred from the presence there of remnants of silicified gravel, and there is a possibility that the flows may have continued much farther north, for kaolinized dykes are seen in railway-cuttings in the parish of Callaghan and a dyke of fresh olivine-basalt has been found in a cutting just north of Bredbo River and another in the parish of Bullanamang near the mouth of Long Flat Creek.

Though outside the area surveyed, mention should be made of an occurrence of Tertiary basalt, believed to be older than Pliocene, which caps the ridge forming the watershed between Toll Bar Creek and Umaralla River just south of the Cooma-Umaralla road. It is underlain by alluvial sediments which form a kind of elevated deep lead some 400 feet above the level of the Pliocene basalt in the valley of Toll Bar Creek (Browne, 1933).

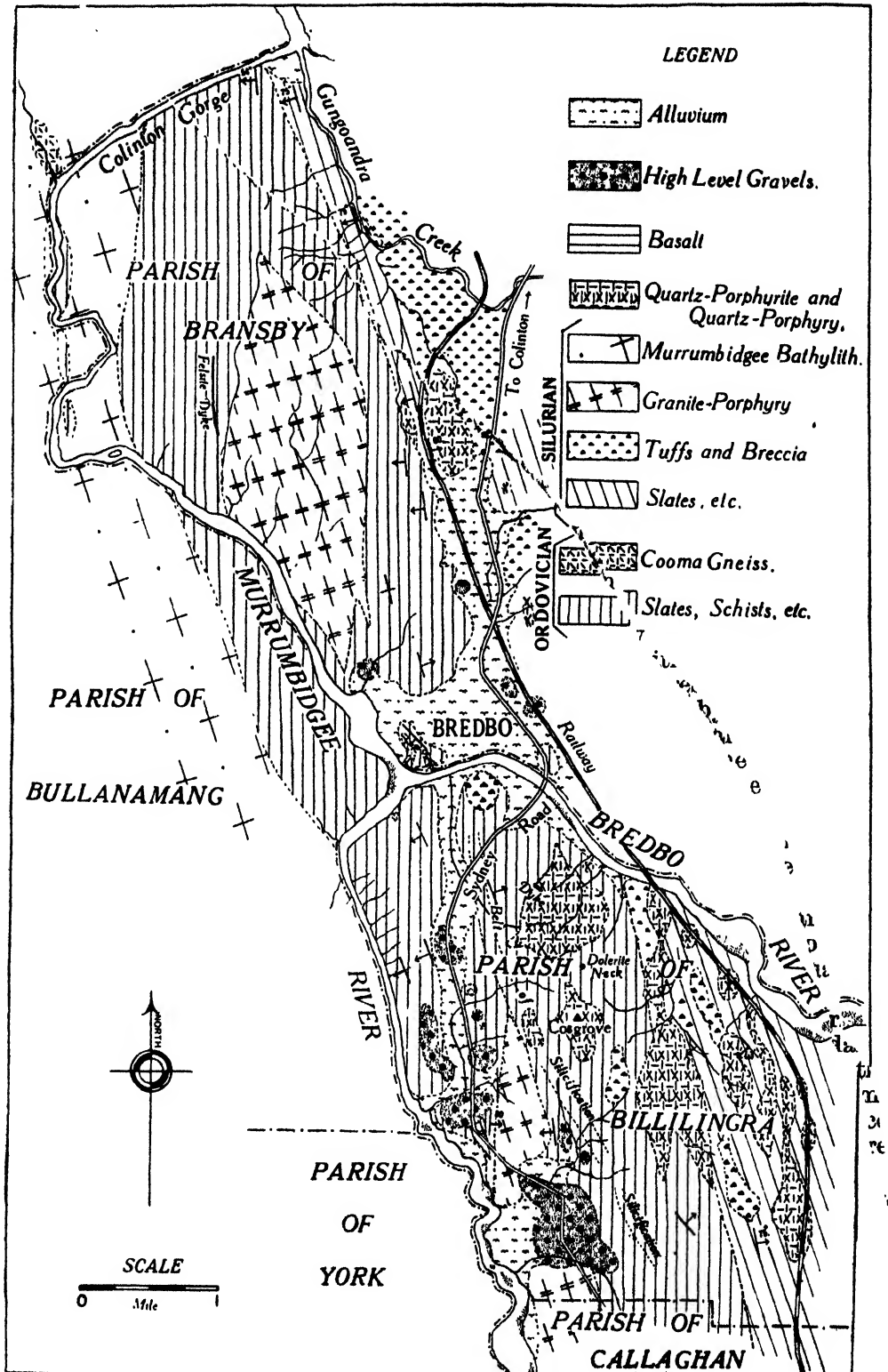


Fig. 1.

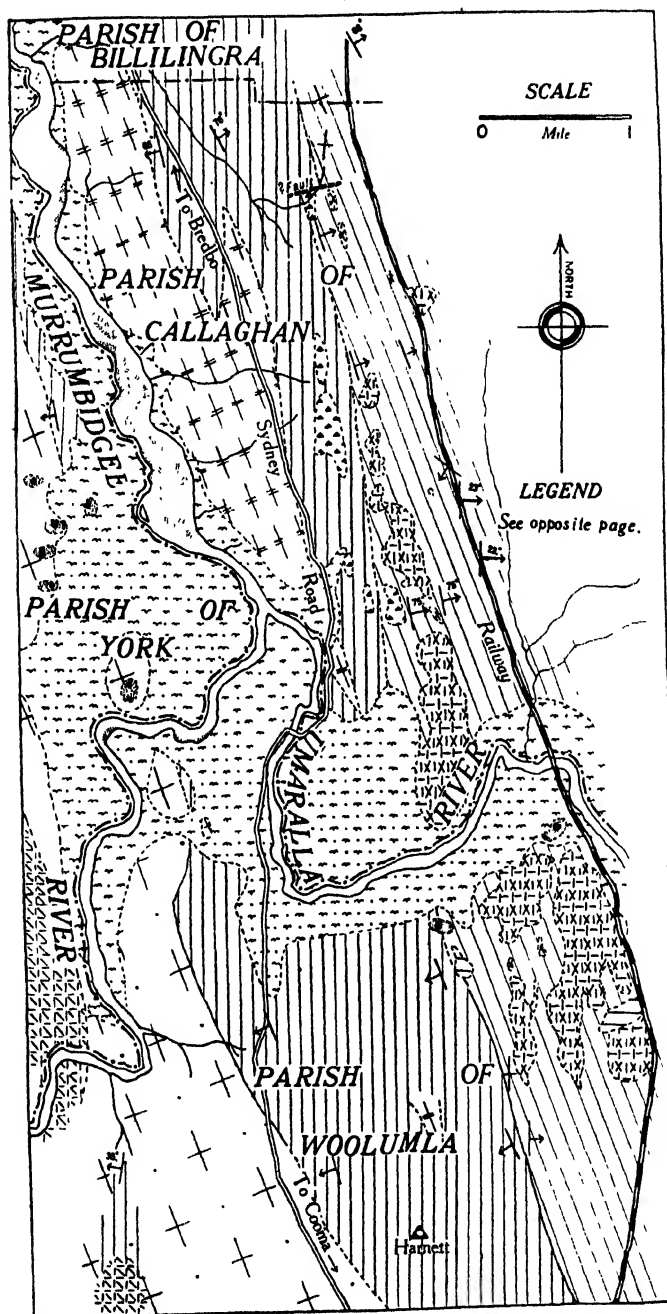


Fig. 2.

Figs. 1 and 2.—Detailed geological map of the eastern half of the Bunyan-Colinton area.

(b) Sediments.

(i) About 100 feet of gravels and ferruginous shales and sandstones underlie the basalts on the ridge east of Toll Bar Creek. In the shales have been found remains of leaves including those of *Cinnamomum* sp.

(ii) Sub-basaltic Pliocene sediments are seen on the Murrumbucka plateau in a tributary of Bulga Creek, where some two or three feet of micaceous grit overlie a small thickness of lignitic or peaty material. Water-bearing sands between basalt-flows have been encountered in sinking wells.

In the eastern part of the area large blocks of cemented gravels or "grey billy" are exposed by the erosion of overlying basalt on the roadside at Pearman's Hill about 170 feet above the Umaralla River. More extensive outcrops appear farther south, north of the road from Cooma to Umaralla and at a height of 100 feet above Toll Bar (Rock Flat) Creek. These are the rock-types referred to in the 1914 paper as quartzitic conglomerate, whose origin was not then understood.

(iii) At many points along the Murrumbidgee and Umaralla Rivers there are banks and terraces of high-level gravels. These are particularly abundant along the Murrumbidgee in the parishes of Billilunga and York and in the village of Bredbo. They are at varying heights above the river, but most of them at about 240, 150 and 70 or 80 feet. The exact age of these is uncertain; the highest and oldest as well as the lower deposits contain pebbles of basalt and grey billy, which would suggest that they postdate the Pliocene basalt, but in view of the existence of older Tertiary basalt-flows referred to above such an inference is not altogether justified.

(iv) Gravels and flood-plain silts, clearly of Recent age, are found at 20 or 25 feet above river-level. They are extensively developed in the Umaralla River valley and along the mature stretches of the Murrumbidgee. Alluvium is found also along many of the tributary creeks in the eastern half of the area, in places as much as 20 feet deep, and considerable quantities of detritus have been spread along the bases of the ridges, partly alluvial, partly colluvial. Gullying, which is unfortunately very widespread, reveals sections showing that these deposits have been to some extent cemented.

IGNEOUS INTRUSIONS.

(a) The Cooma Gneiss.

In the south the chief outcrop of this intrusion is in and around the town of Cooma; over to the west there are numbers of lenses and sills intimately penetrating the Ordovician schists. Northward the intrusion is continued as two more or less well defined parallel zones of granitic penetration, one on either side of the ridge that stretches from Mittagang Bridge to Murrumbucka Gap. The zones are separated by a belt of granitized rock—chiefly mottled gneiss and granulite—that caps the ridge and forms the watershed between the Murrumbidgee on the east and Pilot and Murrumbucka Creeks on the west. The igneous rock is massive as a rule and devoid of directional structures, so that it is a granite rather than a gneiss, and in many places it forms conspicuous tors. Where it is in narrow lenses, however, it has been crushed and granulated and has developed a rude submeridional cleavage which is thought to have been imposed on it at the time of the epi-Silurian diastrophism. On account of the intimate nature of the penetration it is impossible to lay down definite boundaries to the igneous zones, and the outcrops have been marked on the map (Plate VI) only wherever they have been observed in the course of the survey. The petrography of the rock—a contaminated granite—has been fully described by Dr. Joplin.

Both zones of granite are cut off just south of Murrumbucka Gap by the Murrumbidgee batholith, but remnants of it enclosed in the latter and generally

accompanied by granitized schist can be seen at intervals far to the north, as in Sandy (Reedy) Creek and in Gap Creek at the head of the Colinton gorge. The most westerly observed occurrence forms an isolated outcrop in Barkersdale Creek about a furlong up from where it is crossed by the blue gneiss.

Along the western margin there are occasional dykes and lenses of an acid or aplitic modification; these crop out on the Murrumbucka Road near Mittagang Bridge, and at various points among the schists to the north. A few large masses are enclosed in the blue gneiss near Oakvale homestead and there is a little on Barkersdale Creek. It is noteworthy that *lit-par-lit* injection of the adjacent schists, so conspicuous about Cooma, is virtually absent to the north, though it has been observed to a slight extent in association with the more easterly belt of Cooma gneiss.

As to the shape of the intrusion the impression gained is that the numerous lenses and sills are upward projections from an underlying solid mass forming a synchronous bathylith with a very marked submeridional trend and a cross-section roughly approximating that suggested in the 1914 paper, or perhaps a tabular mass with a general dip to the east and many projections into the roof. The extension of the metamorphic effects on the western side of the intrusive axis and their sharp decline on the east, together with the presence of acid modifications on the west, suggest that the progress of the magma was influenced by pressure from the east.

The age of the intrusion is considered to be probably closing Ordovician because of its close relation to the folding and metamorphism of the Ordovician rocks, which was clearly accomplished before the deposition of the Silurian strata.

(b) *The Murrumbidgee Bathylith* (see Plate VI).

Reconnaissance has shown that this extends for about 60 miles north from Cooma, so that only its southern half comes into the present survey. It is the dominating formation in the western half of the area mapped, but since much of it, in the parishes of York and Bullanamang, is in a region uninhabited, untraversed by roads or tracks, and in places mountainous, uncleared and rising to more than 2,000 feet above the river, its detailed study is a matter of some difficulty.

To the south the intrusion frays out into a number of tongues, but near Murrumbucka Gap these coalesce, and in the area mapped the bathylith has a known width of nearly five miles; farther north it is considerably wider.

The eastern margin of the mass is marked by a considerable development of acid rock, mapped separately in 1914 but not differentiated in the present survey. Two types are recognized, one with much pink felspar and some mica and the other aplitic in constitution and devoid of mica. The former seems in places to grade westward into the normal blue gneiss, and the latter, occasionally veined with bright green epidote, appears as sheets or sills arranged subparallel to the margin of the intrusion. Immediately west of the acid phases the prevailing rock-type is a well-foliated primary gneiss with the constitution of a quartz-mica-diorite; westward the foliation becomes less marked and the rock acquires a little potash-felspar in addition to plagioclase.

Dykes and veins of tourmaline-pegmatite and quartz-tourmaline rock, some of which contain a graphic quartz-tourmaline intergrowth, are not uncommon. Along both its margins the gneiss contains numerous elongated and lenticular inclusions, principally of schist on the west and of schist and granulite, Cooma gneiss, and amphibolite and hornblende-granulite on the east. The margins are in general smooth, but modified by concordant tongues and apophyses, and there are intrusive marginal lenses of gneiss amid the invaded rocks. Indeed in some places, as to the east of the river in the parish of Woolumla

and again farther north along the river in the parish of York, the igneous mass might almost be regarded as consisting of great numbers of lenses or sills separated by screens of country-rock.

The Murrumbidgee bathylith is clearly unrelated to the regional metamorphism of the Ordovician rocks and was evidently injected long after this was accomplished; nevertheless it has induced a limited amount of alteration in the invaded rocks. This is most evident along the eastern margin, where it seems to have consisted chiefly of partial or complete metasomatism. Granitization of slates and phyllites is particularly well seen in the parishes of Woolumla and Bransby, and where the Ordovician porphyroids are in contact with the gneiss they have been locally hardened by introduction of quartz and have had their feldspars albitized, though here, as elsewhere, the zone of evident alteration is surprisingly narrow.

Along the western boundary of the mass from Barkersdale Creek into the high country lying to the north some contact-hardening of the invaded schists seems to be indicated, for these form the ridge that has determined the course of the creek, and the country occupied by the gneiss falls away to the east (Fig. 3).

The primary gneissic foliation of the rock and the eastern selvage of acid gneiss and metasomatized country-rock suggest strongly the effects of magmatic differentiation determined by horizontal pressure directed from the west, and acting on a magma already partially crystallized. The resemblance to the occurrences described by Barrow from the Scottish Highlands (Barrow, 1892 and 1893) is heightened by the rounded appearance of some of the plagioclase in the quartz-diorite gneiss.

That compression was renewed after consolidation is indicated by cataclastic structure, particularly in the acid phases. In places the shearing of the gneiss has been very intense.

The characteristics of the intrusion enumerated above reveal it as a bathylith of the synchronous type, though differing in a number of respects from the Cooma bathylith. In detail, however, its structure is rather puzzling, and in particular the shape of its cross-section as deduced from surface-indications. Thus we find that along the western limb the foliation dips consistently to the east, in places at angles as low as 20° and even less. That these dips are those of the mass as a whole is indicated between Barkgunyah and Barkersdale Creeks where the dipping boundary shows well the characteristic relation of outcrop to contour. On the other hand the eastern limb and its extensions dip steeply to the west. The western limb forms relatively low ground and passes beneath the main ridge of granitized schist and Cooma gneiss that extends north from Mittagang Bridge, but near Murrumbucka Gap it rises to overtop the ridge of older rocks. The narrow middle tongue of blue gneiss projecting south from the Gap forms a valley-depression, and its foliation is vertical or dips steeply under another ridge of Cooma gneiss lying to the east. This is seen to be underlain on the other side by the eastern limb of the intrusion. Farther north where the various tongues have coalesced the foliation on the east dips west with increasing steepness till it becomes vertical, and then takes on an easterly dip with a value gradually declining towards the western margin, the vertical position being attained about three-quarters of a mile from the eastern edge. An attempt is made in Fig. 3 to represent these facts semi-diagrammatically.

It would appear on a survey of the available evidence that the intrusion is trough-shaped, and there is a suggestion that the trough is pitching to the south. However these conjectures—for they are little else—relate only to the southern part of the intrusion, and to the surface-outcrops, and no conclusions are justified as to the shape of the mass in cross-section at depth, though it should be pointed out that the easterly dip of the western margin has been observed over a vertical range of nearly 1,500 feet.

The general structural similarity between the bathylith and the Ordovician rocks it invades is noted below. It seems certain that the shape assumed by the intrusion was conditioned by either folding or faulting, and it may well be that the fanning out or deployment of the magma as it made its way up was directed by structural features of the enclosing Ordovician strata, which at that time probably formed the floor of the Silurian geosyncline.

Within the area examined the bathylith is enclosed entirely by Ordovician rocks, but many miles further north it invades the Silurian beds as well. From the structural peculiarities which distinguish it from the massive granites of Devonian and Carboniferous times it is considered to have been injected during the epoch of folding that closed the Silurian period.

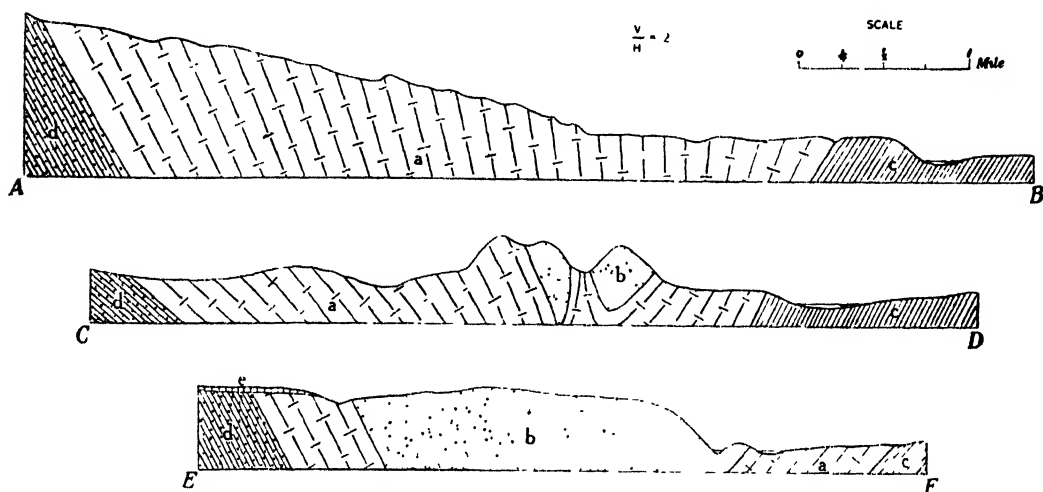


Fig. 3.—Sections across the Murrumbidgee bathylith (Plate VI) to show its structure.

a=bathylith; b=Cooma gneiss and granulite with undetermined dip; c=slates, phyllites, etc., of the eastern belt; d=schists and granulites; e=Tertiary basalt. Datum line about 2,000 ft. above sea-level.

(c) *Porphyries and Porphyrites.* (See Figs. 1 and 2.)

A bewildering variety of these rocks has invaded both Ordovician and Silurian beds, and their distinction is not always easy. Reference has already been made to the oldest of them, the sheared porphyry or porphyroid which is prominent as sills and lenses among the Ordovician rocks and which is believed to be of Ordovician age. Others of the intrusions are thought to be Silurian and others again are post-Silurian.

Granite-Porphyries. Along the right bank of the Murrumbidgee are two large lenticular masses of porphyry enclosed by Ordovician strata, the more southerly upwards of six miles and the other three miles long. The rock is distinguished by containing abundant large bipyramidal phenocrysts of quartz up to three-eighths of an inch in length and rather smaller idiomorphic white feldspars, with biotite and occasional hornblende. Much of the very altered phenocrystal feldspar appears to be plagioclase, but the finely granular groundmass contains orthoclase, and the rocks, though possibly more closely allied to tonalites, may be provisionally called by the general name of granite-porphyry.

The intrusive character of the lenses is obvious in the field from their relations to the Ordovician rocks. The outcrop in the parish of Bransby has

been mapped as a solid mass, but it really appears to be to some extent a congeries of thin lenses or sills.

The rocks have in general suffered shearing or crushing; in the larger intrusions this is mainly peripheral, though in thin section all the rocks are seen to have suffered some strain. Small intrusions of aplite and of coarse pink acid granite or alaskite are closely associated and evidently comagmatic with the porphyries. Apart from the two large intrusions numbers of small ones have been observed, particularly in the parishes of Billilingra and Woolumla, and it has been found that certain of the porphyries occurring at intervals from Bunyan south to Bushy Hill really belong to the same suite. Some of them are massive but others are crushed and may be confused with the porphyroids.

It is noteworthy that these intrusions are arranged parallel to and never very far away (less than a mile) from the Murrumbidgee bathylith. The parallelism is so close as to suggest that the porphyry is comagmatic with the blue gneiss, and this feeling is strengthened by the fact that near its northern end in the Capital Territory the granite of the bathylith merges into granite-porphyry with aplite. Moreover, in the country north of Colinton the porphyry invades Silurian strata. That the porphyry was injected and crushed before the intrusion of the bathylith is shown by the occurrence of a small lens of the latter among the crushed porphyry about a mile north of Billilingra House. The granite-porphyries may thus perhaps be regarded as forerunners of the main bathylith during the epoch of intrusion associated with the late Silurian folding.

Other Porphyries and Porphyrites. The Silurian and Ordovician strata are invaded by a series of minor intrusions of porphyritic rocks. In general they are somewhat dyke-like but so irregular in habit that for the most part it has been possible to map only zones of intrusion and not individual occurrences. Though transgressive in plan, these are seen to be grouped with a rough parallelism to the trend of the invaded *terrain*. One well-defined dyke of felsite north of Por. 93, Par. Bransby has been traced in a direct line for upwards of half a mile. Certain porphyries associated with crystal-tuffs, like some of those in Pors. 23 and 44, Par. Billilingra, are much fractured and show signs of epidotization, silicification, etc., and these may be of Silurian age, contemporaneous with the tuffs; others, perfectly massive to outward showing, would appear to postdate the late Silurian orogenic movements.

Some of the porphyries are readily recognizable as such in hand-specimen, but, as stated above, there are crystal-tuffs which are easily mistaken for igneous rocks, and it would appear that some of these have been mapped as porphyries. In particular parts of the large bifurcate mass depicted west of the railway in parish Billilingra and shown as intersecting both Ordovician and Silurian rocks, have proved to be of crystal-tuff though other parts are definitely of porphyry, and some at least of the fresh, blue rock at Billilingra Siding and north of it is likewise tuff. Again, there are certain types about which, even when examined in thin section, one cannot be quite sure; these have the large resorbed quartz-grains characteristic of porphyries, but their cryptocrystalline groundmass is thickly bestrewn with smaller angular fragments of quartz and felspar, possibly resulting from the invasion of a tuff by a porphyry. A rock of this type constitutes the mass in the Travelling Stock Reserve three-quarters of a mile south of Bredbo and has been mapped as tuff.

Of the true porphyries a number of types may be distinguished in the field. Most common perhaps are those containing abundant phenocrysts of quartz and felspar, with hornblende and sometimes biotite, in a stony groundmass which may vary in colour—bluish, brown or greenish generally. In some types there is little or no megascopic felspar and the quartz phenocrysts are small, and in a few others quartz is missing.

Light-coloured felsitic rocks, some showing flow-banding, are not uncommon. An intrusion of this type forms the rough, bare and prominent Cosgrove Hill in parish Billilingra and is continued in the larger mass immediately to the north. Quartz-felsites and porphyries also seam the Silurian tuff in Por. 23, Par. Billilingra, and these continue north at intervals in the parish of Bransby in the low ground and on the ridge east of the road. Some two miles north of Bredbo is an intrusion of porphyry and felsite between road and railway and a small interformational lens of white felsite shows in a railway-cutting. Narrow sills of the same rock traverse the Silurian tuffs two miles farther north.

The Silurian strata in the parishes of Callaghan and Woolumla are invaded by a series of irregular intrusions, some of which show a brecciform structure, angular fragments of dark blue porphyry up to about 4 inches in length being embedded in a lighter-coloured felsitic matrix, evidently a later cognate intrusion.

No petrographical study of these porphyritic rocks has been made beyond the examination of a few microslides. Felspars in many of them have been altered almost beyond recognition, but plagioclase and orthoclase have both been detected among the phenocrysts. Some of the rocks are probably to be classed as porphyrites but the most acid or felsitic types are true porphyries with dominant alkali-felspar and little or nothing in the way of dark minerals. In certain felsites phenocrystal quartz is almost absent and this mineral is contained mainly in the cryptocrystalline groundmass.

Around the intrusions occasional very local hardening and silicification of the country-rock is to be seen, and the igneous rocks themselves may be traversed by quartz-veins. Indeed it appears probable that quartz as veins was introduced with all or nearly all of the igneous intrusions, both plutonic and hypabyssal, so that Ordovician and Silurian rocks are intersected with them and the surface in places is littered with quartz-fragments.

It is noteworthy that the porphyries and porphyrites appear only in the eastern half of the area. No sign of them has been found west of the eastern margin of the Murrumbidgee bathylith. How far eastward they extend has not been ascertained.

As to the age of these porphyritic rocks all one can say definitely is that they are post-Silurian. Very similar porphyries and porphyrites are known elsewhere which were injected during a diastrophic epoch at the close of Middle Devonian time, and to this the rocks just described may well belong.

(d) Genetic Relations among the Igneous Rocks.

It is interesting to examine the possibilities of consanguinity between the Palaeozoic rocks of the area. The Ordovician amphibolites and sheared rhyolites and tuffs are probably complementary, likewise the rhyolites and basic lavas of the Silurian, and the Ordovician porphyroids may be hypabyssal equivalents of the sheared rhyolites. There is very probably a close genetic relation between the Silurian tuffs, granite-porphyries and intrusive gneisses, and the kinship may even extend to the post-Silurian porphyries, porphyrites and felsites. Indeed the region may have been a petrological province from Ordovician to Devonian time, but in the absence of detailed chemical and petrological studies such a suggestion is little more than speculation.

(e) Quartz-Dolerites.

A few minor dolerite intrusions of indeterminate age have been noted. One of these, possibly a small volcanic neck, breaks through the Ordovician rocks in Por. 34, Par. Billilingra and a smaller one cuts the Silurian beds in the adjoining Por. 23. An east-west dyke cutting through blue gneiss near its eastern margin occurs in a tributary of Spring Vale Creek, and a number of other

similar dykes were found in the course of traverses across the Murrumbidgee bathylith west of Bredbo, one of which, just west of the south-west corner of Por. 40, Par. Bullanamang, has a width of 12 yards and extends for at least half a mile in a direction about W. 15° S. Some of the dykes have basaltic margins and it is possible that a few small dykes of basalt without olivine, noted in the north-west of Par. Billilingra, may belong to the same series.

Under the microscope the rocks are seen to belong to the quartz-dolerite kindred. Some of them have uralitized augite and rather plentiful biotite with interstitial quartz and micropegmatite; others though devoid of quartz, betray their affinities by the presence of pigeonitic pyroxene.

These rocks are of quite a different petrological type from the Tertiary basic rocks, which they probably antedate, but apart from this and the fact that they are post-Silurian nothing is known as to their geological age. They may possibly be related to other similar rocks which have been found scattered through the highlands (Browne, 1933).

GEOLOGICAL STRUCTURE OF THE PALÆOZOIC ROCKS.

The elucidation of the structure of both Ordovician and Silurian rocks is somewhat difficult, largely because there are few good natural sections across the strike. Moreover the Ordovician rocks have all acquired schistosity or cleavage, and the lavas and tuffs of the eastern zone have no bedding-planes, while the Silurian rocks are largely massive tuffs, and shales which have taken on an imperfect cleavage. No beds have been detected whose repetition might provide a key to the Silurian structure, and it is not even quite certain if the beds in contact with the Ordovician are at the base of the sequence. It is for these reasons that no attempt has been made to estimate thicknesses of strata.

In the eastern half of the area many of the dips are high and many more are vertical, hence it is not surprising that with the same strike changes in dip-direction are relatively common; in the circumstances these changes have little or no significance.

The Ordovician belt in its extreme western parts has a predominance of easterly dips, which may be as low as 40° . On the east high westerly dips are the rule, though they may be down to 65° . In the south of the parish of Murrumbucka along Pilot Creek persistent westerly dips occur, but the beds turn over again very quickly and slope to the east near Mittagang Bridge and along the Murrumbidgee downstream from it. This minor anticline is on the line of that observed south of the Murrumbidgee along Spring Creek, and what is possibly its northern continuation is seen in the schists up along Barkersdale Creek west of the blue gneiss.

It would thus appear that the Ordovician strata have been thrown into a rather asymmetrical syncline modified by the subsidiary Pilot Creek anticline.

The coming in of the Murrumbidgee bathylith to some extent obliterates and disturbs the folding of the beds, but the structure indicated by the foliation of the blue gneiss, as noted above, is broadly synclinal. Actually the folding of the Ordovician rocks was probably synclinorial rather than synclinal, with smaller crumplings superimposed on the main folds.

This interpretation of the structure, if correct, would make the Coolringdon beds lying to the west and east older than the more metamorphosed Binjura beds in the middle. This does not accord with the views of Dr. Joplin, who places the beds in the reverse relation and considers that the Cooma gneiss was injected not into a syncline but into an anticline. Of course the present structure is to be regarded as the result of both the late Ordovician and the late Silurian diastrophism, but how far the latter was effective in modifying the attitude of the rocks it would be hard to say. The slates and chloritic phyllites may well have suffered further deformation along with the Silurian sediments, and indeed

such a condition is suggested by the apparent dipping of Silurian under Ordovician beds in the parish of Bransby, but it is most unlikely that any new folding could have been imposed on the recrystallized and rigid granulites and granitized schists, especially when stiffened by the intrusive Cooma gneiss, and the broadly synclinal structure within which the latter is contained at Cooma is therefore probably to be regarded as original—that is to say, Ordovician. On the other hand, since the Ordovician rocks presumably formed the floor of the geosyncline in which the Silurian beds were deposited, it is reasonable to suppose that the folding of the latter by pressure from the west was accompanied by and related to disruption and faulting of the older rocks, and this may be in part responsible for their present attitude, though it must be said that no traces of such dislocation have been observed.

The Silurian rocks have not been examined for any great distance across their strike, so that little is known about their structure. In the most westerly beds there is perhaps a preponderance of easterly dips, but in the parish of Bransby this is reversed. Dips are as a rule fairly high and may be vertical, due in part to the fact that the beds in contact with the Ordovician rocks are practically everywhere soft and easily deformed shales, though indeed the tuffs are also in places on end. Low angles were noted only in sandstones some distance away from the boundary in the parish of Callaghan.

It is possible that the more resistant units of the series are broadly and gently folded while the weaker shales have been thrown into minor isoclinal folds. This view appears to be supported by the result of a reconnaissance trip along the road from Cooma to Umaralla; about two miles east of Rock Flat Creek some open folding of ripple-marked shales and sandstones was observed and farther on some smaller folds in shale, while the repeated occurrence of bars of brown quartzite suggested folding of these beds on a major scale.

STRUCTURAL RELATIONS OF ORDOVICIAN AND SILURIAN ROCKS.

This is another question whose solution is hampered by the absence of clear-cut sections across the strike and by the fact that the Silurian slates have been folded along approximately the Ordovician axes. Moreover, in a number of places the actual boundary cannot be exactly defined owing to a covering of soil, or where, as in the parish of Woolumla, there are weathered Ordovician and Silurian slates in apposition. Nevertheless it is indisputable that a big chronological hiatus exists between the two series, representing Lower and probably Middle Silurian time, and the difference in degree of alteration between the Silurian slates and tuffs and the sheared Ordovician tuffs and lavas points to a major tectonic break, but whether overthrust or angular unconformity is not easy to say. Along the boundary the Silurian in places dip east off the Ordovician strata, elsewhere both sets of beds dip east, while again the Silurian may be seen dipping west and the Ordovician east. The fact that many of the dips are high discounts the value of the observations, but in the parish of Bransby the westerly dip of both Ordovician and Silurian rocks is rather constant and probably significant.

There is a small but definite discordance in strike between the two formations which is particularly noticeable in the parish of Bransby, where the Silurian trend is in general about 15° or 20° west of north and parallel to the boundary, while that of the Ordovician is almost meridional. As a result the Ordovician beds are very gradually truncated northwards, so that beyond the limits of the map the Silurian slates are in contact with the porphyroids, the sheared rhyolites and tuffs having disappeared.

The available evidence, though inconclusive, would seem to point to an angular unconformity rather than a faulted junction, with the possibility that

overturning of the plane of unconformity was accomplished locally through thrusting or folding from the west during the late Silurian diastrophism.

It is of interest that in the Yass district, some 80 miles north of Bredbo, Sherrard (1939) and Brown (1941) have figured an angular unconformity between highly cleaved and steeply dipping Upper Ordovician strata and overlying Middle (?) Silurian beds, which are there only very moderately folded.

SUMMARY.

In continuation of Part I, published in 1914, the geology of a belt of country some 20 miles in meridional extent has been mapped and examined. The Palæozoic formations are Upper Ordovician and Upper Silurian, both containing igneous as well as sedimentary material. There are also remains of Tertiary basalt-flows and Tertiary and Recent sediments.

The Ordovician beds are invaded by late Ordovician granite, to which is due in part their metamorphism, and by a late Silurian bathylith with satellitic granite-porphyrries, and both Ordovician and Silurian strata are cut by numerous intrusions of porphyry and porphyrite, and by quartz-dolerites.

The geological structure of the Palæozoic rocks is discussed and the structural relations of the Silurian and Ordovician formations. It is thought probable that these are separated by an angular unconformity.

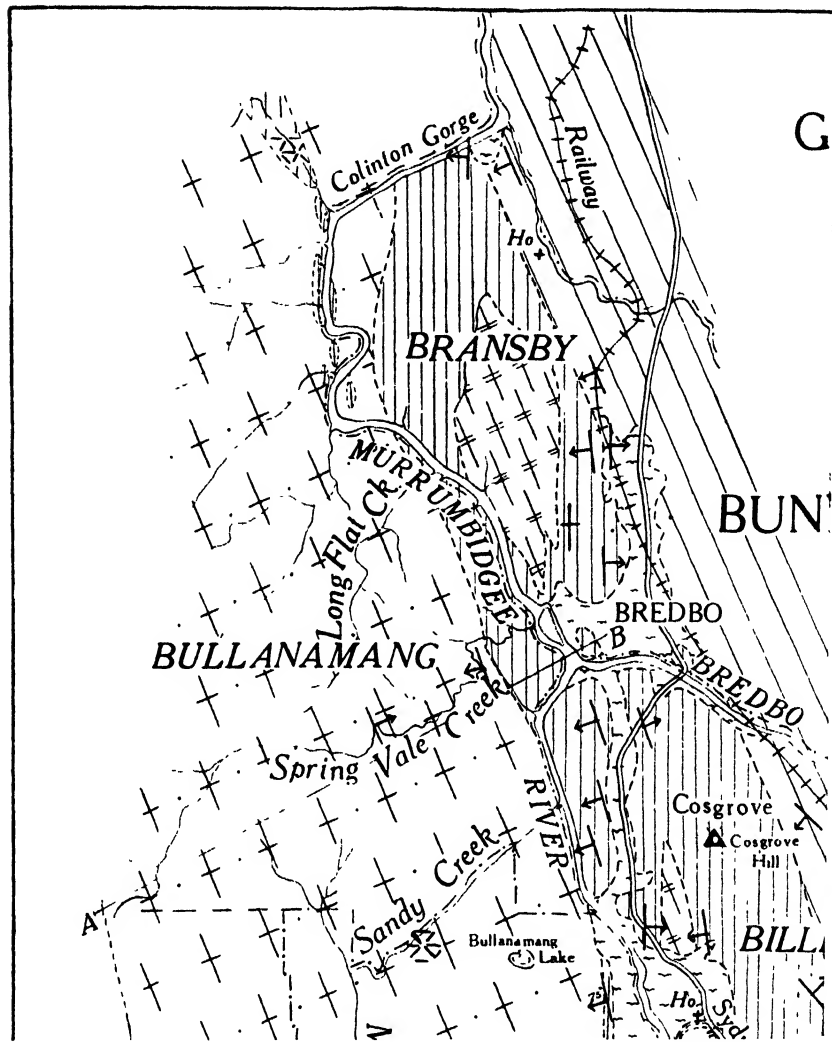
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EXPLANATION OF PLATE.

Geological Map of the Country between Bunyan and Colinton.

Note.—Dips shown within the Murrumbidgee bathylith are those of the foliation of the gneiss.



OBITUARY NOTICES.

JAMES ADAM DICK was born at Windsor, N.S.W., and died at the age of 76 in December, 1942. He graduated in Arts at the University of Sydney in 1886, and then proceeded to Edinburgh, where he obtained the degrees of Bachelor of Medicine and Master of Surgery in 1891, his Doctorate of Medicine in 1892, and Fellowship of the Royal College of Surgeons, Edinburgh, in 1901.

In 1893 Dr. Dick returned to Australia, and began practice at Randwick, where he remained until he died, and where he had a large practice and a high reputation as a medical man. He was always actively concerned in advancing the interests of the British Medical Association, and held office in various capacities, including that of President. He was for a number of years a member of the Medical Board of N.S.W., and a Councillor of St. Andrew's College, University of Sydney, from 1925 to 1937. He was Honorary Medical Officer of the Home for Aged and Infirm, Randwick, and of the Asylum for Children.

Dr. Dick was on active service in the Boer War, from 1899 to 1902, and in the Great War from 1914 to 1919. He was mentioned in dispatches, and was made a Companion of the Most Distinguished Order of St. Michael and St. George. As commanding officer of a base hospital in France he enjoyed the respect and confidence of those serving under him. The records of the Royal Society show that he always had a keen interest in its affairs, and attended its meetings and functions regularly. On several occasions he even sent greetings to the President and members from his base hospital in France. He joined the Royal Society in 1894, and from 1898 to 1901 was Joint Honorary Secretary of its Medical Section.

Dr. Dick was known and respected by medical men throughout Australia, and it has been said of him that "he showed in his everyday life those qualities of heart and hand which are credited to the true follower of Æsculapius and he was prepared to spend much of his life and energy in maintaining at a high standard the corporate life of the profession which he adorned".

GERALD HARNETT HALLIGAN was born on 21st April, 1856, and died at Killara on 23rd November, 1942. He was for many years a supervising engineer in the Department of Public Works of New South Wales, and was concerned with harbour and river construction work. He was especially an authority on tides and currents, of which he made a life study, not only round the coasts of Australia, but of the world. A number of maps were compiled by him in connection with the Oceanography Section of the Pacific Science Congresses. For some years Mr. Halligan was Government Hydrographer of New South Wales. He accompanied the third Expedition organized by the Royal Society of London, to Funafuti, and was in charge of the boring operations, which proved very successful. The results of the expedition were published in 1904 by the Royal Society of London, in the volume "The Atoll of Funafuti". Mr. Halligan joined the Royal Society in 1880, and at the time of his death was the oldest member but one, having had an unbroken membership of sixty-two years.

KELSO KING, who died on 7th February, 1943, in his ninetieth year, was born in Sydney on 30th December, 1853. His first training was on a Queensland station as jackeroo, but he soon returned to the city, where he entered the banking business as a junior in the Bank of New South Wales. He later joined

the Commercial Banking Company of Sydney, where he later became a manager, and an inspector. He also became a director of the Bank of New South Wales. He was managing director of the Mercantile Mutual Insurance Company, of which he had been chief executive officer since its inception in 1877; and of the Australian General Insurance Company; Chairman of Directors of Mort's Dock and Engineering Company; a director of the Colonial Mutual Life Assurance Society, and of the Australian Fertiliser Company, and of many other companies.

His public and philanthropic activities were legion, and he was associated, in the capacity of chairman and president, with such organizations as the Walter and Eliza Hall Trust, the St. John Ambulance Association, and Brigades, and the Royal Life Saving Society. He always had a keen and sympathetic interest in the youth of the State, and was closely associated with the Boy Scouts' Association—one of the oldest Scout Troops in the State bears the designation "Sir Kelso King's Own"—and the Navy League. He was a member of the Council of The King's School, the Canberra Grammar School, and Trinity Grammar School. Sir Kelso was a member of the Australasian Pioneers' Club. In recognition of his many services of a public and philanthropic nature, he was created a Knight Bachelor in 1929.

ARCHIBALD DURRANT OLLÉ was born at Beyton, Suffolk, England, on 23rd November, 1868, and died on 9th September, 1942, at Ashfield, N.S.W. Ollé joined the British Navy as a signalman in 1883, and left England in the brig *Nautilus* in 1886. In Sydney he joined H.M.S. *Nelson* and later H.M.S. *Calliope*, the only ship which escaped from Apia Harbour, Samoa, on the historic occasion of the hurricane which burst so suddenly that all other ships, including several warships of other nations, were wrecked and swept ashore. Ollé contracted malaria which resulted in his discharge from the Navy in 1888.

He entered the service of the Hamilton Hospital, Victoria, and later entered the Sydney Hospital under Dr. Muskett. His hospital experience enabled him to undertake private work, and he travelled with patients to England on many occasions.

He visited Vienna and worked in Germany for two years, returning to Sydney, where he set up a practice in massage, electrotherapy and radiology in 1899, in which he continued until his death.

MARCUS BALDWIN WELCH, who died at the age of 47 on 29th September, 1942, was born at Palmerston North, New Zealand, and came to Sydney in 1906. He was educated at Fort Street and Sydney Boys' High Schools, and in 1916 graduated at the University of Sydney with first-class Honours in Chemistry, and the University Medal in Botany. On leaving the University he joined the A.I.F., but was discharged by order of the Minister for Defence for special work in explosives in Great Britain. On returning to Australia he was appointed Demonstrator in Botany at the University of Sydney. In August, 1919, he joined the staff of the Sydney Technological Museum, as Assistant Economic Botanist, remaining there until he was transferred to the Forestry Commission in 1936. During 17 years at the Technological Museum, Mr. Welch carried out very valuable researches in the physical and mechanical properties of Australian timbers, and the results were published in the *Journal and Proceedings of the Royal Society of N.S.W.* Thirty-nine papers in all were contributed by Mr. Welch to the Journal.

He was also author and co-author of several Bulletins of the Sydney Technological Museum.

On joining the Forestry Commission Mr. Welch was appointed Senior Research Officer in the Division of Wood Technology, where he rendered excellent service to the timber industry of the State. The rapid development of the

Division in a comparatively short time was largely due to the energy, initiative and organizing ability of Mr. Welch. He also rendered useful service to the Standards Association of Australia in the preparation of standard specifications for timber.

During the present war Mr. Welch's work was chiefly connected with defence matters, such as testing timber for aeroplanes and rifle stocks, and experimenting with timbers for producer gas units. He became Chairman of the Producer Gas Committee, and of the Charcoal Research Committee.

Mr. Welch was a member of the Royal Society from 1920 until his death, and held office on the Council from 1931 to 1941, and as Honorary Treasurer for 1939 and 1940. He could not be persuaded to accept the office of President, believing that his official post would prevent him from giving the necessary time to the work entailed. His sudden death while on a holiday in the Blue Mountains came as a great shock to his friends and colleagues, who will remember him for his friendly nature, his simplicity, integrity and conscientious attention to his work, in which he never spared himself. In fact his assiduous attention to his work since the war began probably contributed in part to his early death.

ABSTRACT OF PROCEEDINGS
OF THE
Royal Society of New South Wales

April 7th, 1943.

The Annual Meeting, being the six hundred and third General Monthly Meeting of the Society, was held in the Hall of Science House, Gloucester and Essex Streets, Sydney, at 7.45 p.m.

The President, Professor Priestley, was in the chair. Sixty-one members and eleven visitors were present. The minutes of the previous meeting were read and confirmed.

The following were elected officers and members of the Council for the coming year :

President :

A. B. WALKOM, D.Sc.

Vice-Presidents :

PROF. H. PRIESTLEY, M.D., Ch.M., B.Sc.
IDA A. BROWN, D.Sc.

A. BOLLIGER, Ph.D., A.A.C.I.
H. S. HALCRO WARDLAW, D.Sc., F.A.C.I.

Hon. Secretaries :

PROF. A. P. ELKIN, M.A., Ph.D.

D. P. MELLOR, M.Sc.

Hon. Treasurer :

A. CLUNIES ROSS, B.Sc., F.C.A. (*Aust.*).

Members of Council :

G. H. BRIGGS, D.Sc., Ph.D., F.Inst.P.
J. A. DULHUNTY, B.Sc.
F. P. J. DWYER, M.Sc.
F. LIONS, B.Sc., Ph.D., A.I.C.
W. H. MAZE, M.Sc.

J. E. MILLS, M.Sc., Ph.D.
F. R. MORRISON, A.A.C.I., F.C.S.
G. D. OSBORNE, D.Sc., Ph.D.
H. H. THORNE, M.A., B.Sc., F.R.A.S.
H. W. WOOD, M.Sc., A.Inst.P., F.R.A.S.

The Annual Balance Sheet and Revenue Account were submitted to members by the Honorary Treasurer, and on the motion of Mr. A. Clunies Ross, seconded by Dr. A. Bolliger, were adopted.

**THE ROYAL SOCIETY OF NEW SOUTH WALES.
BALANCE SHEET AS AT 28th FEBRUARY, 1943.**

1942.		LIABILITIES.			1943.			
£			£	s.	d.	£	s.	d.
	Trust Funds—							
	Clarke Memorial Fund—							
	Balance as at 28th February, 1942	..	1,790	1	3			
	Add Interest for year ended 28th							
	February, 1943	71	12	0			
			£1,861	13	3			
	Less Expenses—							
	Lecture Fee	£26 5 0						
	Printing Lecture ..	32 10 0						
	Printing Tickets and Cir-							
	culars and Advertising	3 10 1						
	Engraving	0 12 6						
				62	17	7		
						1,798	15	8
	Walter Burfitt Prize Fund—							
	Balance as at 28th February, 1942	..	663	16	5			
	Add Interest for year ended 28th							
	February, 1943	26	11	0			
						690	7	5
	Liversidge Bequest—							
	Balance as at 28th February, 1942	..	700	3	8			
	Add Interest for year ended 28th							
	February, 1943	28	0	0			
			£728	3	8			
	Less Expenses—							
	Lecture Fee	£31 10 0						
	Travelling Expenses..	11 2 11						
	Printing Tickets and Cir-							
	culars and Advertising	4 14 6						
				47	7	5		
						680	16	3
3,154							3,169	19 4
14	Subscriptions Paid in Advance					6	6 0
94	Provision for Unexpired Proportion of Life Membership Subscriptions						92	0 0
27,820	Accumulated Fund					28,284	0 4
	Contingent Liability—In connection with perpetual Leases granted to the Australian National Research Council and the Pharmaceutical Society of New South Wales.							
£31,082							£31,552	5 8

1942.		ASSETS.		1943.	
£				£	s. d.
	Cash at Bank and on Hand—				
	The Union Bank of Australia Ltd.		410	19	8
	Commonwealth Savings Bank of Australia		54	18	6
280	Petty Cash		4	1	3
				469	19 5
	Bonds and Inscribed Stock—				
	Bonds (Face Value £1,000)	1,011	5	0	
8,839	Stock (Face Value £8,060)	8,027	11	3	
				9,038	16 3
	Science House Management Committee—				
14,650	Payments to date			14,756	0 0
	Sundry Debtors—				
	Subscriptions Unpaid	193	9	0	
—	Less Reserve	193	9	0	
6,800	Library			6,800	0 0
	Furniture	458	19	5	
	Less Depreciation written off	22	19	5	
459				436	0 0
	Pictures	39	10	4	
	Less Depreciation written off	2	0	4	
39				37	10 0
	Lantern	14	14	0	
	Less Depreciation written off	0	14	0	
15				14	0 0
£31,082				£31,552	5 8

The above Balance Sheet has been prepared from the books of account, accounts and vouchers of The Royal Society of New South Wales, and is a correct statement of the position of the Society's affairs on the 28th February, 1943, as disclosed thereby. We have obtained certificates showing that the whole of the Bonds and Inscribed Stock are held by the Society's bankers for safe keeping.

Prudential Building,
39 Martin Place,
Sydney, 15th March, 1943.

HORLEY & HORLEY,
Chartered Accountants (Aust.).

(Sgd.) A. CLUNIES ROSS,
Hon. Treasurer.

REVENUE ACCOUNT FOR THE YEAR ENDED 28th FEBRUARY, 1943.

Year ended 28th Feb., 1942.		Year ended 28th February, 1943.	
£		£ s. d.	£ s. d.
4	To Advertising	—	—
36	„ Cleaning	36	0 0
25	„ Depreciation	25	13 9
11	„ Electric Light	7	6 3
15	„ Insurance	14	12 6
36	„ Library Maintenance	56	14 9
63	„ Miscellaneous Expenses	45	8 0
292	„ Office Salaries and Audit Fees	305	9 6
29	„ Office Sundries and Stationery	21	9 8
164	„ Printing	82	4 3
453	„ Printing and Publishing Journal	267	16 5
6	„ Repairs	—	—
55	„ Stamps and Telegrams	58	6 8
16	„ Telephone	20	14 9
1,205		—	941 16 6
683	„ Balance, being Net Revenue for the Year, transferred to Accumulated Fund		481 5 9
£1,888			£1,423 2 3

Year ended 28th Feb., 1942.		Year ended 28th February, 1943.	
£	£	£ s. d.	£ s. d.
504	By Members' Subscriptions		485 2 0
800	„ Government Subsidy		400 0 0
325	„ Science House Receipts	315	0 0
42	„ Less Rent Paid	35	1 8
—	283		279 18 4
74	„ Miscellaneous Receipts		38 13 4
324	„ Interest Received	322	11 7
	Less—		
	Clarke Memorial Fund	£71	12 0
	Walter Burfitt Prize Fund	26	11 0
	Liversidge Bequest	28	0 0
127		126	3 0
—	197		196 8 7
30	„ Proportion of Life Members' Subscriptions		23 0 0
£1,888			£1,423 2 3

ACCUMULATED FUND ACCOUNT FOR THE YEAR ENDED
28th FEBRUARY, 1943.

1943—February 28—		£ s. d.
To Arrears of Subscriptions, written off		21 0 0
„ Balance, carried down		28,284 0 4
		£28,305 0 4
1942—February 28—		£ s. d.
By Balance from last Account		27,819 15 7
1943—February 28—		
By Amount Transferred from Bad Debts Reserve Account		3 19 0
„ Net Revenue for the Year		481 5 9
		£28,305 0 4
1943—February 28—		
By Balance, Brought Down		£28,284 0 4

The Annual Report of the Council (1942-43) was read, and on the motion of Professor Elkin, seconded by Mr. R. W. Challinor, the report was adopted.

REPORT OF THE COUNCIL, 1942-1943 (RULE XXVI).

We regret to report the loss by death of seven members since April 1st, 1942: James Adam Dick (1894), John Clifford Firth (1935), Gerald Harnett Halligan (1880), Sir Kelso King (1896), Archibald Durrant Ollé (1913), Marcus Baldwin Welch (1920), and Sir Joseph J. Thomson, an Honorary Member since 1915.

By resignation the Society has lost six members: Harry Williams, Francis W. Firth, Thomas H. Tennant, Stanley W. E. Parsons, Harold Tindale and Robert T. Wade. During the year, fifteen members with a continuous membership of thirty-five years were elected to life membership, without further payment of fees, namely Frank Lee Alexander, Charles Anderson, Horatio Scott Carslaw, Henry Harvey Dare, James Adam Dick, Edward William Esdaile, Mark Foy, Henry Ferdinand Halloran, George Harker, Sir Kelso King, Charles A. L. Loney, Arthur Marshall McIntosh, Cecil Purser, Oscar Ulric Vonwiller, and Walter George Woolnough.

Seven new members have been elected during the year, and the membership now stands at 292. The new members are Jack Leslie Still, Desmond J. Brown, John Conrad Jaeger, Neville Allan Gibson, Raymond Norman Matthew Lyons, Gordon Roy Williams and Arthur Lippman. Several members are on active service abroad, others are with the home forces. Brigadier H. B. Taylor has been reported prisoner of war in Malaya. Many of our members are engaged in important war work and on research connected with the war effort.

In conformity with the resolution passed during 1941, no Annual Dinner was held during 1942.

Eleven ordinary meetings of Council and one special meeting have been held during the year beginning April 1st, 1942, at which the average attendance was 14.

Attendances of individual members of Council have been as follows: Professor H. Priestley, 11; Dr. Ida Brown, 11; Mr. J. A. Dulhunty, 11; Dr. F. Lions, 11; Professor A. P. Elkin, 10; Mr. W. H. Maze, 10; Mr. F. R. Morrison, 10; Dr. A. Bolliger, 9; Mr. F. P. J. Dwyer, 9; Dr. J. E. Mills, 9; Mr. D. P. Mellor, 8; Dr. G. D. Osborne, 8; Mr. H. H. Thorne, 8; Dr. H. S. H. Wardlaw, 7; Mr. E. J. Kenny, 6; Mr. A. Clunies Ross, 6; Dr. C. H. Briggs, 5; Dr. A. B. Walkom (elected August), 5; Dr. C. Anderson (resigned July), 1. Number of meetings: 11.

During the same period nine general meetings have been held, with an average attendance of 33.

Twenty-eight papers were accepted for reading and publication, and a short talk on "The Native Peoples of the Australian Territories" was given by Professor A. P. Elkin.

Symposium.—At the monthly meeting in July, a symposium on Rubber was held, the following being the speakers and subjects:

"Some Important Natural Rubber Resources", D. H. Priestley (Manager, Dunlop Rubber Company's Factory).

"Some Aspects of the Chemistry of Natural and Synthetic Rubber", F. Lions, B.Sc., Ph.D.

"Production and International Control of Rubber", W. H. Maze, M.Sc.

"Possible Plant Sources of Rubber in Australia", F. R. Milthorp.

Great interest was shown in the subject, and over sixty members and visitors were present, a number of whom took part in the discussion which followed the addresses.

Popular Science Broadcasts.—Owing to war-time conditions, including the very restricted lighting in the city and suburbs, it was thought advisable to dispense with the usual series of Popular Science Lectures, as it was considered that the attendance would be limited, and would not justify invitations to busy scientists to deliver lectures. Instead it was proposed to have a series of broadcast talks from the Australian Broadcasting Commission. The Commission responded cordially to the suggestion, and four broadcasts were given during July, as follows:

July 7th.—"Vitamins and the Loaf of Bread", Professor H. Priestley, M.B., Ch.M.

July 14th.—"Chemical Wonders: Glass from Coal, Rubber from Petroleum", A. R. Penfold.

July 21st.—"Minerals in Peace and War", G. D. Osborne, D.Sc.

July 28th.—"Chemical Harvest of the Sea", D. P. Mellor, M.Sc.

Clarke Memorial Lecture.—The lecture for 1942 was delivered by Mr. E. C. Andrews on May 21st, and the subject was "The Heroic Period of Geological Work in Australia".

Clarke Memorial Medal for 1942.—The Medal was awarded to Dr. William Rowan Browne, of the University of Sydney, for his research work during past years, and also for his work in preparing for publication a large amount of material left by the late Sir Edgeworth David for the book on the Geology of the Commonwealth, on which Sir Edgeworth had been working for some years before his death.

Liversidge Lecture.—Two lectures were delivered under the Liversidge Bequest, by Dr. J. S. Anderson, Senior Lecturer in Inorganic Chemistry in the University of Melbourne, as follows:

October 27th.—“The Chemistry of the Earth.”

October 29th.—“The Imperfect Crystal.”

Galileo-Newton Tercentenary.—This double historical anniversary was commemorated at the meeting of October 7th, and an address entitled “Galileo and Newton: Their Times and Ours” was given by Professor O. U. Vonwiller. There was an attendance of fifty-seven.

Finance.—The audit of the Society's accounts discloses that the finances are in a satisfactory condition.

Government Grant.—A government grant from the Government of New South Wales of £400 for the year 1943 has been made.

Science House.—The Royal Society's share of the profits on Science House during the period April 1st, 1942–March 31st, 1943, has been £315. From this, however, must be deducted the cost of the air-raid shelter which was built in the Small Hall in order to comply with National Security Regulations. The Royal Society's share of the cost was £106.

In accordance with the regulations it was necessary for the glass to be removed from the doors of the Council Room and of the office, and to be replaced with masonite. The windows in the Society's rooms facing Gloucester Street were treated by covering them with cellophane to prevent splintering in case of air raids.

Time of General Meetings.—Owing to the “black-out” conditions in city and suburbs, it was decided to hold the general meetings at an earlier hour, and the hours of 4.30 and 6.30 were tried at successive meetings. This alteration did not prove popular, and resulted in a great decrease in attendance. It was resolved to revert to the hour of 7.45.

Science House Management Committee.—The Royal Society has been represented at meetings of the Science House Management Committee by Mr. M. B. Welch and Mr. A. R. Penfold, with Dr. G. D. Osborne and Dr. C. Anderson as substitute representatives. On the death of Mr. Welch, Dr. G. D. Osborne was appointed as representative and Mr. Clunies Roos as substitute representative. On the resignation of Dr. C. Anderson, Dr. F. Lions was appointed as substitute representative in his place.

Alteration of Rules.—The committee appointed to consider the rules and make recommendations as to their revision met on a number of occasions and considered the question of revision of each rule very thoroughly. The revised rules were finally approved, and have now been printed and distributed to members. It is hoped that by this revision the rules have been made clearer and that a number of inconsistencies which existed have been removed.

Purchase of Periodicals and Binding.—The amount of £29 13s. 9d. has been spent on purchasing periodicals during the year under review, and the amount of £27 1s. has been spent on binding. The total amount expended on the library was thus £56 14s. 9d. A number of volumes are still at the binders, and others are prepared and waiting to go.

Exchanges.—The number of exchanges sent has been still further reduced, and now stands at 221, chiefly within the British Empire. It is possible still to send to South America, Mexico, Hawaii, the United States, Palestine, Russia, Spain and Switzerland. A few societies have asked that our Journal be held for them and sent after the war, and such societies are holding their publications back also until such time as they can be safely forwarded. It is noteworthy, however, that only a small number of periodicals seem to have been lost in transit since the war began.

Accessions.—For the twelve months ended February the number of accessions entered in the catalogue is 1,741 parts of periodicals and 88 whole volumes.

Borrowers and Readers.—Members and visitors reading in the library during the year numbered thirty-five. The number of books and periodicals borrowed by members, institutions and accredited readers was eighty-one. Among the institutions which made use of the arrangements for inter-library borrowing were: Standards Association of Australia, National Standards Laboratory, National Museum, Melbourne, the Universities of Sydney, Queensland and Melbourne, Division of Economic Entomology, Canberra, Food Preservation Laboratory, Homebush, MacMaster Laboratory, Sydney, The Colonial Sugar Refining Co., the Australian Gas Light Company, Amalgamated Wireless Limited, the Public Works Department, Sydney, the Department of Home Security, and the Sydney County Council.

General.—In accordance with decisions taken at the end of 1941, further numbers of old text-books were given to the Medical School, Botany Department and Geology Department in the University of Sydney. Some extra shelf accommodation is thus available, but it will be necessary to take still further action to dispose of duplicates and books which are not needed in a periodical library, in order to make room for the increase of periodicals year by year.

Recommendations.—It is recommended that the Council proceed with the proposed scheme of making the libraries of the Royal Society and the Linnean Society of New South Wales complementary.

The deaths were announced of the following members : Dr. James Adam Dick, a member since 1894, and Sir Kelso King, a member since 1896.

The certificates of three candidates for admission as ordinary members of the Society were read for the first time.

The certificate of a candidate for admission as an ordinary member of the Society was read for the second time. The following person was duly elected an ordinary member of the Society : William Kevin McCoy.

Clarke Memorial Medal.—The announcement was made of the award of the Clarke Memorial Medal for 1943 to Dr. W. L. Waterhouse.

Election of Auditors.—On the motion of Professor Elkin, seconded by Mr. Challinor, Messrs. Horley and Horley were re-elected auditors to the Society for 1943-44.

Library.—The following donations were received : parts of periodicals, 557 ; 35 whole volumes, and 202 back numbers.

The President, Professor H. Priestley, delivered his address, entitled " Life and Living ".

Professor Priestley then installed Dr. A. B. Walkom as President for the year 1943-44. Dr. Walkom thanked the members for the honour they had done him in electing him President. He then called upon Dr. Lions to propose a vote of thanks to the retiring President for his address and his work for the Society during his term of office. This was carried by acclamation.

The following papers were read by title only :

" Nova Puppis 1942 ", by H. W. Wood, M.Sc., A.Inst.P., F.R.A.S.

" A Polyhedral Model of the Projection Plane ", by F. A. Behrend. (Communicated by Professor H. S. Carslaw.)

May 5, 1943.

The six hundred and fourth General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. A. B. Walkom, was in the chair. Twenty-three members and two visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of three candidates for admission as ordinary members were read for the first time.

The certificates of three candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : William Dudgeon, Ronald Arthur Plowman, and Leonard Winch.

Library.—The following donations were received : 88 parts of periodicals, six whole volumes and eight back numbers.

Correspondence.—A letter was received from Buckingham Palace, conveying the sincere thanks of His Majesty the King and the Duchess of Kent, for sympathy in the death of the Duke of Kent.

The following paper was read :

" Preliminary Notes on Solution-cracking Treatment of Torbanite ", by J. A. Dulhunty, B.Sc.

Lecturette.—A lecturette on " Reflections of Light from Film-Covered Glass Surfaces " was given by Mr. J. Bannon, B.Sc.

June 2, 1943.

The six hundred and fifth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. A. B. Walkom, was in the chair. Thirty-three members and one visitor were present. The minutes of the previous meeting were read and confirmed.

The death was announced of Dr. James Edward Mills, a member since 1940.

The certificates of three candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : Thomas Iredale, Ivan Stewart Turner and Jean Annie Kimble.

Clarke Memorial Lecture.—It was announced that the Clarke Memorial Lecture for 1943 would be delivered at Science House on June 23rd, by Dr. H. G. Raggatt, the title being " Australia's Mineral Industry in the Present War ".

Library.—The following donations were received : 85 parts of periodicals and seven whole volumes.

The following papers were read :

" Tabulata and Heliolitida from the Wellington District, N.S.W. ", by O. A. Jones, M.Sc. (Communicated by Dr. Ida A. Brown.)

" The Etch Figures of Basal Sections of Quartz : Their Use in the Orientation of Water-worn Crystals ", by F. N. Hanlon, B.Sc., Dip.Ed.

Lecturettes.—The following lecturettes were given :

“Evaporated Metal Films”, by F. P. J. Dwyer, M.Sc.

“Biotin”, by Professor H. Priestley, M.D., Ch.M., B.Sc.

Popular Science Lectures.—The Popular Science Lectures for 1943 were announced, as follows :

Thursday, June 17th.—“How We Came to Stand Upright”, by Professor Harvey Sutton, O.B.E., M.D., Ch.B., D.P.H., B.Sc.

Thursday, July 15th.—“Veterinary Science and the Community”, by H. Parry, B.A.

Thursday, August 19th.—“Exploring the Inside of the Earth”, by Professor L. A. Cotton, M.A., D.Sc.

Thursday, September 16th.—“Soviet Research on Applied Botany”, by Professor E. Ashby, D.Sc., A.R.C.S., D.I.C.

Thursday, October 21st.—“Architecture : The Setting for Life”, by Professor L. Wilkinson, F.R.I.B.A., F.R.A.I.A.

July 7, 1943.

The six hundred and sixth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. A. B. Walkom, was in the chair. Twenty-seven members and two visitors were present. The minutes of the previous meeting were read and confirmed.

The certificate of a candidate for admission as an ordinary member was read for the first time.

Library.—The following donations were received : 87 parts of periodicals and three whole volumes.

Commemoration of the Bi-centenary of the Birth of Sir Joseph Banks.—The meeting was devoted to commemoration of the bi-centenary of the birth of Sir Joseph Banks, and an address, entitled “Sir Joseph Banks and Australia”, was given by Dr. G. Mackaness, M.A.

August 4, 1943.

The six hundred and seventh General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. A. B. Walkom, was in the chair. Fifty members and four visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of four candidates for admission as ordinary members of the Society were read for the first time.

The certificate of a candidate for admission as an ordinary member of the Society was read for the second time. The following person was duly elected an ordinary member of the Society : Reginald John Nelson Whiteman.

Library.—The following donations were received : 180 parts of periodicals and 44 whole volumes.

The following papers were read :

“An Elementary Proof of R. A. Fisher’s Distribution of the Coefficient of Normal Correlation with Some Introductory Notes on Correlation and Regression”, by D. T. Sawkins, M.A., B.A. (Read by title only.)

“The Production of Hyoscyamine from *Duboisia* Species—

Part I. “Methods of Quantitative Estimation”, by J. A. Lean, M.P.S., and C. S. Ralph, B.Sc.

Part II. “Extraction of the Base”, by C. S. Ralph, B.Sc., and J. L. Willis, B.Sc.

Exhibit.—Mr. D. P. Mellor showed an exhibit : A New Source of Light : the Fluorescent Lamp.

Lecturette.—Dr. F. Lions gave a lecturette, entitled “Penicillin and Gramicidin”.

September 1, 1943.

The six hundred and eighth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, 157 Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. A. B. Walkom, was in the chair. Twenty-four members and two visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of three members for admission as ordinary members of the Society were read for the first time.

The certificates of four members for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society : Robert Desider Louis Frederick, Ernest Patrick Molloy, John William George Neuhaus and James Foote Walker.

Library.—The following donations were received: 81 parts of periodicals and four whole volumes.

The following papers were read:

"Studies on Colour Reactions for Sugars. Part I. The Identification and Determination of Monosaccharides with Thymol, Hydrochloric Acid and Ferric Chloride", by A. Bolliger, Ph.D.

"Ebonite as a Radiometer. Part I. The Distortion of Ebonite by Long Infra-red Radiations and New Methods of Radiation Measurement", by G. G. Blake, F.Inst.P., M.I.E.E.

Lecturette.—A lecturette was given by Mr. H. H. Thorne on "Edmund Halley".

October 6, 1943.

The six hundred and ninth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. A. B. Walkom, was in the chair. Thirty-five members and visitors were present. The minutes of the previous meeting were read and confirmed.

The death was announced of Dr. John Job Crew Bradfield, a member since 1922.

A certificate of a candidate for admission as an ordinary member of the Society was read for the first time.

The certificates of three candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Mrs. Daphne Luber, Howard Hamlet Gordon McKern and John Kenneth Moore Simpson.

Library.—The following donations were received: 88 parts of periodicals and four whole volumes.

Presentation of the Clarke Memorial Medal.—The President presented the Clarke Memorial Medal for 1943 to Dr. Walter Lawry Waterhouse, for his great services to science, especially his studies of rust in wheat.

The following papers were read:

"The Chemistry of Bivalent and Trivalent Iridium. Part I. Compounds of Bivalent Iridium Halides with Tertiary Arsines", by F. P. Dwyer, M.Sc., and R. S. Nyholm, M.Sc.

"Stringocephalid Brachiopoda in Eastern Australia", by Ida A. Brown, D.Sc.

Lecturette.—A lecturette on "The Future of the Native Peoples of the South-west Pacific" was given by Professor A. P. Elkin.

November 3, 1943.

The six hundred and tenth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. A. B. Walkom, was in the chair. Thirty-eight members, four visitors, and a guest speaker, Dr. Cowlshaw, were present. The minutes of the previous meeting were read and confirmed.

The death was announced of Sir Archibald Howie, a member since 1936.

The certificates of two candidates for admission as ordinary members of the Society were read for the first time.

The certificate of a candidate for admission as an ordinary member of the Society was read for the second time. The following person was duly elected an ordinary member of the Society: Alexander Campbell Nicol.

Royal Society's Medal.—It was announced that the Royal Society's Medal had been awarded to Mr. Edwin Cheel for his contributions in the field of botanical research, and to the advancement of science in general.

Library.—The following donations were received: 101 parts of periodicals, six whole volumes and 18 back numbers.

The following paper was read:

"The Vibrations of Square Molecules. Part I. The Normal Coordinates and Vibration Frequencies of Planar AB_4 Molecules", by Allan Maccoll, M.Sc.

Celebration of 400th Anniversaries.—The meeting was chiefly devoted to the celebration of the 400th anniversary of the publication of two works:

"De Revolutionibus Orbium Coelestium", Libri VI, by Copernicus and

"De Humani Corporis Fabrica" (Libri Septem), by Vesalius.

An address on Copernicus was given by the Rev. Father D. J. K. O'Connell and one on Vesalius was given by Dr. Leslie Cowlshaw. Both addresses were illustrated with lantern slides.

December 1, 1943.

The six hundred and eleventh General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. A. B. Walkom, was in the chair. Thirty-two members and one visitor were present. The minutes of the previous meeting were read and confirmed.

The certificates of two candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected as ordinary members of the Society: Barbara Joyce Burfitt and John Stanton Burkitt.

Library.—The following donations were received: 108 parts of periodicals and nine whole volumes.

Presentation of Royal Society's Medal.—The President presented the Royal Society's Medal to Mr. Edwin Cheel.

The following papers were read:

"Further Determination of Specialisation in Flax Rust caused by *Melampsora lini* (Pers.) Lév.", by W. L. Waterhouse, D.Sc.Agr., and I. A. Watson, Ph.D., D.Sc.Agr.

This paper was read by title only in the unavoidable absence of both the authors.

"A Study of the Magnetic Behaviour of Complexes Containing the Platinum Metals", by D. P. Mellor, M.Sc.

"The Geology of the Cooma District, N.S.W. Part II: The Country between Bunyan and Colinton", by W. R. Browne, D.Sc.

ABSTRACT OF PROCEEDINGS

OF THE SECTION OF

GEOLOGY

Chairman : Dr. W. R. Browne.

Honorary Secretary : Mr. J. A. Dulhunty.

Eight meetings were held during the year 1943, the average attendance being twelve members and three visitors.

Meetings.

April 16th.—Annual Meeting. Election of Office-bearers for 1943 : Chairman, Dr. W. R. Browne, and Honorary Secretary, Mr. J. A. Dulhunty.

Business : Exhibits : By Mr. Lambeth : Defects in glass due to formation of metamorphic minerals during processing. By Mr. Dulhunty : Rich torbanite from Marangaroo, assaying 236 gallons of oil per ton. Address by Dr. W. R. Browne, "Origin and History of the Tasman Geosyncline". The structure persisted from Cambrian to Permian time, after which it lacked geographical continuity and moved westward.

May 21st.—Address by Mr. C. A. Sussmilch, "The Physiographic Criteria of Faulting, with Special Reference to Eastern Australia". Distinction was made between monoclinal fold scarps and true fault scarps. Evidence of faulting was detailed, and the application of physiographic criteria to problems in Eastern Australia was discussed.

June 18th.—Address by Mr. J. A. Dulhunty, "Recent Research on the Nature and Origin of Coal, with some applications to New South Wales". Theories for the differentiation of organic debris into coals of different type and rank. The influence of environment of accumulation. Constitution of coals. Metamorphism of coal-forming debris. Applications to New South Wales coals.

July 16th.—Address by Mr. W. H. Maze, "Landform Analysis from Topographic Maps". Frequency of occurrence of surfaces at different levels, generalised contours, true profiles, and applications to the Bathurst district were discussed.

August 20th.—Address by Mr. F. N. Hanlon, "Piezo-electric Quartz". The address dealt with properties, uses, sources of supply, technique in processing, and orientation by means of etched surfaces.

September 17th.—Exhibits and Notes : By Dr. Brown : Devonian brachiopods from eastern Australia. By Miss Crockford : A mid-palaeozoic ostracod fauna from the Yass district. By Dr. Osborne : An illustration of spiral garnets. By Miss Quodling : Surface oxidation and tarnish of some minerals. By Mr. Kenny : Oil shale from Mount Kembla. By Mr. Lambeth : Note on currents in tanks of molten glass and similar phenomena in nature. By Dr. Browne : Gneissic granites from Cooma, Tharwa, Wheeo, Adelong and Kosciusko.

October 15th.—Address by Dr. G. D. Osborne, "Recent Researches in Experimental Geology and their Significance". An account was given of the work of Bridgman on the influence of high temperatures and pressures on minerals, also the researches of Griggs, and the contributions by Daley to geophysics.

November 19th.—Exhibit by Dr. Osborne : Quartzite pebble from Upper Kuttung tillite of Dunn's Creek.

Address by Dr. I. A. Brown, "The Permian Problem : Recent Researches affecting Australian Correlations". Reference was made to results of the Permian Conference during the XVIIth International Geological Congress, Moscow, U.S.S.R., 1937, and recent research on Permian problems in Australia and other parts of the world.

INDEX.

A	Page.
Abstract of Proceedings.. ..	xxi
Section of Geology	xxxi
Annual Report and Balance Sheet ..	xxii
Australia's Mineral Industry in the Present War	52
Awards of—	
Clarke Memorial Medal for 1942 ..	xxv
Clarke Memorial Medal for 1943 ..	xxvii
Royal Society's Medal	xxix

B	
Balance Sheet	xxii
Behrend, F. A.—	
A Polyhedral Model of the Projective Plane	20
Bequest, Form of	v
Blake, G. G.—	
Ebonite as Radiometer. The Dis- tortion of Ebonite by Long Infra- red Radiations	106
Bolliger, A.—	
Studies on Colour Reactions for Sugar. Part I	109
Brachiopoda in Eastern Australia, Stringocephalid	119
Brown, I. A.—	
Stringocephalid Brachiopoda in Eastern Australia	119
Browne, W. R.—	
The Geology of the Cooma District, N.S.W. Part II	156
Burfitt Prize	xx

C	
Chemistry of Bivalent and Trivalent Iridium. Part I. Compounds of Bivalent Iridium Halides with Tertiary Arsines	116
Clarke Memorial Lecture—	
Australia's Mineral Industry in the Present War	52
Clarke Memorial Medal	xxv
Colour Reactions for Sugars, Studies on	109
Complexes Containing the Platinum Metals, A Study of the Magnetic Behaviour of	145
Compounds of Bivalent Iridium Halides with Tertiary Arsines	116
Cooma District, N.S.W., The Geology of. Part II. The Country Between Bunyan and Colinton	156

P

D	Page.
Duboisia Species, Production of Hy- oscyamine from—	
Part I. Methods of Quantitative Estimation	96
Part II. Extraction of the Base ..	99
Dulhunty, J. A.—	
Preliminary Notes on Solution Crack- ing Treatment of Torbanite ..	24
Dwyer, F. P., and Nyholm, R.S.—	
Chemistry of Bivalent and Trivalent Iridium. Part I. Compounds of Bivalent Iridium Halides with Tertiary Arsines	116

E	
Ebonite as Radiometer	106
Etch Figures of the Basal Sections of Quartz: Their Use in the Orienta- tion of Water-worn Crystals ..	40
Exhibits	xxviii

F	
Flax Rust, Further Determinations of Specialisation in, Caused by <i>Melampsora Lini</i> (Pers.) Lév. ..	138
Further Determinations of Specialisation in Flax Rust Caused by <i>Melampsora</i> <i>Lini</i> (Pers.) Lév.	138

G	
Geology of the Cooma District, N.S.W. Part II. The Country Between Bunyan and Colinton	156
Government Grant	xxvi
Guide to Authors	v

H	
Hanlon, F. N. —	
The Etch Figures of Basal Sections of Quartz: Their Use in the Orienta- tion of Water-worn Crystals ..	40

I	
Infra-red Radiations, Distortion of Ebonite by Long	106
Iridium, Chemistry of Bivalent and Trivalent Iridium. Part I ..	116

	Page.
Jones, O. A.— <i>Tabulata</i> and <i>Heliolitida</i> from the Wellington District, N.S.W. ..	33

L

Lean, J. A., and Ralph, C. S.— Production of Hyoscyamine from <i>Duboisia</i> Species. Part I. Methods of Quantitative Estimation ..	96
Part II. Extraction of the Base ..	99
Lecturettes	xxviii
Life and Living	2
List of Members	ix

M

Maccoll, Alan— Vibration of Square Molecules. Part I	130
Magnetic Behaviour of Complexes Con- taining the Platinum Metals ..	145
<i>Melanpsora Lini</i> (Pers.) Lév., Further Determinations of Specialisation Caused by	138
Mellor, D. P.— A Study of the Magnetic Behaviour of Complexes containing the Platinum Metals	145
Members, List of	ix
Mineral Industry in the Present War, Australia's	52
Monosaccharides, Identification and De- termination of with Thymol, Hydro- chloric Acid and Ferric Chloride	109

N

Nova Puppis, 1942	17
Nyholm, R. S.—See Dwyer, F. P. ..	116

O

Obituaries	173
Officers for 1943-44	xxi

P

Platinum Metals, A Study of the Magnetic Behaviour of Complexes containing	145
Polyhedral Model of the Projective Plane	20
Popular Science Broadcasts	xxv
Preliminary Notes of Solution Cracking Treatment of Torbanite	24
Presidential Address. H. Priestley ..	1
Priestly, H.—Presidential Address ..	1
Production of Hyoscyamine from <i>Duboisia</i> Species. Part I	96
Production of Hyoscyamine from <i>Duboisia</i> Species. Part II	99
Projective Plane, Polyhedral Model of the	20

Q

	Page.
Quartz, Etch Figures of Basal Sections of	40

R

Radiometer, Ebonite as	106
Raggatt, H. G.— Australia's Mineral Industry in the Present War. Clarke Memorial Lecture	52
Ralph, C. S.—See Lean, J. A.	96
Ralph, C. S., and Willis, J. L.— Production of Hyoscyamine from <i>Duboisia</i> Species. Part II. Ex- traction of the Base	99
Regression and Correlation, Simple ..	85
Report of Council, 1942-1943	xxv
Revenue Account	xxiv

S

Sawkins, D. T. - Simple Regression and Correlation ..	85
Simple Regression and Correlation ..	85
Society's Medal and Money Prize ..	xix
Square Molecules, Vibrations of ..	130
Stringocephalid Brachiopoda in Eastern Australia	119
Studies on Colour Reactions for Sugars. Part I. Identification and Deter- mination of Monosaccharides with Thymol, Hydrochloric Acid and Ferric Chloride	109
Symposium on Rubber	xxv

T

<i>Tabulata</i> and <i>Heliolitida</i> from the Wellington District, N.S.W.	3
Torbanite, Preliminary Notes on Solution- cracking Treatment of	24

V

Vibrations of Square Molecules. Part I. The Normal Coordinates and Vibra- tion Frequencies of Planar AB ₄ Molecules	130
---	-----

W

Walter Burfitt Prize	xx
Waterhouse, W. L., and Watson, I. A.— Further Determinations of Specialisa- tion in Flax Rust caused by <i>Melanpsora Lini</i> (Pers.) Lév. ..	138
Water-worn Crystals, Use of Etch Figures of Basal Sections of Quartz in the Orientation of	40
Watson, I. A.—See Waterhouse, W. L. ..	138
Wellington District, N.S.W., <i>Tabulata</i> and <i>Heliolitida</i> from	33
Willis, J. L.—See Ralph, C. S.	99
Wood, H. W.— Nova Puppis, 1942	17

ISSUED APRIL 20, 1945

VOL. LXXVIII

PARTS I-II

JOURNAL AND PROCEEDINGS
OF THE
ROYAL SOCIETY
OF NEW SOUTH WALES

FOR

1944

(INCORPORATED 1881)

PARTS I-II (pp. 1 to 69)

OF

VOL. LXXVIII

Containing Papers read in April, May and July
With Plate I

EDITED BY
THE HONORARY SECRETARIES

THE AUTHORS OF PAPERS ARE ALONE RESPONSIBLE FOR THE
STATEMENTS MADE AND THE OPINIONS EXPRESSED THEREIN



SYDNEY
PUBLISHED BY THE SOCIETY, SCIENCE HOUSE
GLOUCESTER AND ESSEX STREETS

1945

CONTENTS

VOLUME LXXVIII

Parts I-II

	Page.
ART. I. —Presidential Address. By A. B. Walkom, D.Sc. (Issued August 30, 1944) ..	1
ART. II. —Extension of Maxwell's Equations. By P. Foulkes, B.Sc. (Issued August 30, 1944)	14
ART. III. —Some Lower Cretaceous Foraminifera from Bores in the Great Artesian Basin, Northern New South Wales. By Irene Crespin, B.A. (Communicated by Dr. Ida. A. Brown.) (Issued August 30, 1944)	17
ART. IV. —A Note on the Role of the Nitrosyl Group in Metal Complexes. By D. P. Mellor, M.Sc., and D. P. Craig, M.Sc. (Issued August 30, 1944)	25
ART. V. —The Geomorphology of the Central Eastern Area of New South Wales. Part I. Methods of Landform Analysis from Topographic Maps. Part II. Landform Analysis of the Orange-Bathurst District. By Wilson H. Mazo, M.Sc. (Issued October 27, 1944)	28
ART. VI. —Clarke Memorial Lecture. The Relationship of the Australian Continent to the Pacific Ocean—Now and in the Past. By W. H. Bryan, M.C., D.Sc. (Issued October 27, 1944)	42
ART. VII. —Notes on the Nomenclature and Taxonomy of Certain Species of <i>Melaleuca</i> . By Edwin Cheel. (Issued November 22, 1944)	63
ART. VIII. —The Chemistry of Bivalent and Trivalent Rhodium. Part VII. Complexes with Diethyl Sulphide. By F. P. Dwyer, M.Sc., and R. S. Nyholm, M.Sc. (Issued November 22, 1944)	67

JOURNAL AND PROCEEDINGS
OF THE
ROYAL SOCIETY
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CONTENTS

VOLUME LXXVIII

Parts I-II *

	Page.
ART. I.—Presidential Address. By A. B. Walkom, D.Sc. (Issued August 30, 1944) ..	1
ART. II.—Extension of Maxwell's Equations. By P. Foulkes, B.Sc. (Issued August 30, 1944)	14
ART. III.—Some Lower Cretaceous Foraminifera from Bores in the Great Artesian Basin, Northern New South Wales. By Irene Crespin, B.A. (Communicated by Dr. Ida. A. Brown.) (Issued August 30, 1944)	17
ART. IV.—A Note on the Role of the Nitrosyl Group in Metal Complexes. By D. P. Mellor, M.Sc., and D. P. Craig, M.Sc. (Issued August 30, 1944)	25
ART. V.—The Geomorphology of the Central Eastern Area of New South Wales. Part I. Methods of Landform Analysis from Topographic Maps. Part II. Landform Analysis of the Orange-Bathurst District. By Wilson H. Maze, M.Sc. (Issued October 27, 1944)	28
ART. VI.—Clarke Memorial Lecture. The Relationship of the Australian Continent to the Pacific Ocean—Now and in the Past. By W. H. Bryan, M.C., D.Sc. (Issued October 27, 1944)	42
ART. VII.—Notes on the Nomenclature and Taxonomy of Certain Species of <i>Melaleuca</i> . By Edwin Cheel. (Issued November 22, 1944)	63
ART. VIII.—The Chemistry of Bivalent and Trivalent Rhodium. Part VII. Complexes with Diethyl Sulphide. By F. P. Dwyer, M.Sc., and R. S. Nyholm, M.Sc. (Issued November 22, 1944)	67

Part III †

ART. IX.—The Light Absorption and Magnetic Properties of Nickel Complexes. By H. A. McKenzie, D. P. Mellor, and the late J. E. Mills and L. N. Short. (Issued December 7, 1944)	70
ART. X.—Bessel's Formula in Relation to the Calculation of the Probable Error from a Small Number of Observations. By R. C. L. Bosworth, Ph.D., F.A.C.I. (Issued December 7, 1944)	81
ART. XI.—Review of Analyses of Some Australian Fleece Wools. By M. Lipson, B.Sc., A.A.C.I., and Una A. F. Black, B.Sc. (Issued June 15, 1945)	84
ART. XII.—The Bauxites of New South Wales. Their Distribution, Composition and Probable Origin. By F. N. Hanlon, B.Sc., Dip.Ed. (Issued June 15, 1945) ..	94
ART. XIII.—The Determination of Calcite and Aragonite in Invertebrate Shells. By D. M. Bray. (Issued June 15, 1945)	113
ART. XIV.—Quaternary Arsonium Salts and their Metal Co-ordination Compounds. Part I. Bismuth. By F. P. Dwyer, M.Sc., N. A. Gibson, B.Sc., and R. S. Nyholm, M.Sc. (Issued June 15, 1945)	118
ART. XV.—The Sternal Integument of <i>Trichosurus vulpecula</i> . By Adolph Bolliger and Margaret H. Hardy. (Issued June 15, 1945)	122

* Published April 20, 1945.

† Published December 3, 1945.

	Page.
ART. XVI.—Studies in the Phenanthridine Series. Part I. The Cyclisation of 2-Formamido-Diphenyls. By E. Ritchie, M.Sc. (Issued August 10, 1945) ..	134
ART. XVII.—Studies in the Phenanthridine Series. Part II. The Cyclisation of Some 4'-Bromo and 4'-Dimethylamino Acyl-2-Aminodiphenyls. By E. Ritchie, M.Sc. (Issued August 10, 1945) ..	141
ART. XVIII.—Studies in the Phenanthridine Series. Part III. The Influence of the Acyl Group in the Morgan-Walls Reaction and the Mechanism of the Reaction. By E. Ritchie, M.Sc. (Issued August 10, 1945) ..	147
ART. XIX.—Studies in the Phenanthridine Series. Part IV. 1:10-Dimethyl Phenanthridines. By E. Ritchie, M.Sc. (Issued August 10, 1945) ..	159
ART. XX.—Studies in the Phenanthridine Series. Part V. Phenanthridine-6-Aldehyde and Related Compounds. By E. Ritchie, M.Sc. (Issued August 10, 1945) ..	164
ART. XXI.—Studies in the Phenanthridine Series. Part VI. A Synthesis of 3-Methyl Phenanthridine. By E. Ritchie, M.Sc. (Issued August 10, 1945) ..	169
ART. XXII.—Studies in the Phenanthridine Series. Part VII. A Synthesis of Benzo(c)-phenanthridine. By E. Ritchie, M.Sc. (Issued August 10, 1945) ..	173
ART. XXIII.—Studies in the Phenanthridine Series. Part VIII. 3:8-Diamino-Phenanthridine and Related Substances. By E. Ritchie, M.Sc. (Issued August 10, 1945) ..	177
ART. XXIV.—The Physics of Rubbing Surfaces. By F. P. Bowden, Sc.D. (Issued September 7, 1945) ..	187

Part IV *

ART. XXV.—Thermal Conductivity from Measurements of Convection. By R. C. L. Bosworth, Ph.D., F.A.C.I. (Issued February 20, 1946) ..	220
ART. XXVI.—Quaternary Arsonium Salts and their Metal Co-ordination Compounds. Part II. Cadmium. By F. P. Dwyer, M.Sc., N. A. Gibson, B.Sc., and R. S. Nyholm, M.Sc. (Issued February 20, 1946) ..	226
ART. XXVII.—Complexes of Ferric Chloride with Tertiary Arsines. By R. S. Nyholm, M.Sc. (Issued February 20, 1946) ..	229
ART. XXVIII.—The Response of the Sternal Integument of <i>Trichosurus vulpecula</i> to Castration and to Sex Hormones. By A. Bolliger, Ph.D. (Issued February 20, 1946) ..	234
ART. XXIX.—A Polarographic Study of the Isomeric Chromium Sulphates. By J. B. Willis, B.Sc. (Issued February 20, 1946) ..	239
ART. XXX.—The Vibrations of Square Molecules. Part II. The Vibration Frequencies of Planar AB ₃ C ₂ (Trans) Molecules. By A. Maccoll, M.Sc. (Issued February 20, 1946) ..	246
ART. XXXI.—Some Interference Effects with Mica. By O. U. Vonwiller, B.Sc., F.Inst.P. (Issued February 20, 1946) ..	252
ART. XXXII.—A Note on the Magnetic Behaviour of Verdo-Hæmochromogen. By D. P. Craig, M.Sc., and D. P. Mellor, M.Sc. (Issued February 20, 1946) ..	258
ART. XXXIII.—The Chemistry of Bivalent and Trivalent Iridium. Part II. The Standard Oxidation Reduction Potential for the Chloriridite-Chloriridate System in Hydrochloric Acid Solution. By F. P. Dwyer, M.Sc., H. A. McKenzie, B.Sc., and R. S. Nyholm, M.Sc. (Issued February 20, 1946) ..	260
ART. XXXIV.—The Chemistry of Bivalent and Trivalent Rhodium. Part VIII. Rhodic and Rhodous Complexes with Dimethylglyoxime. By F. P. Dwyer, M.Sc., and R. S. Nyholm, M.Sc. (Issued February 20, 1946) ..	266
TITLE PAGE, CONTENTS, NOTICES, PUBLICATIONS ..	i
OFFICERS FOR 1944-45 ..	vii
LIST OF MEMBERS, AWARDS OF MEDALS, ETC. ..	ix
ABSTRACT OF PROCEEDINGS ..	xxi
PROCEEDINGS OF THE SECTION OF GEOLOGY ..	xxxix
INDEX TO VOLUME LXXVIII ..	xxxiii

NOTICE.

THE ROYAL SOCIETY of New South Wales originated in 1821 as the "Philosophical Society of Australasia"; after an interval of inactivity, it was resuscitated in 1850, under the name of the "Australian Philosophical Society", by which title it was known until 1856, when the name was changed to the "Philosophical Society of New South Wales"; in 1866, by the sanction of Her Most Gracious Majesty Queen Victoria, it assumed its present title, and was incorporated by Act of the Parliament of New South Wales in 1881.

 TO AUTHORS.

Particulars regarding the preparation of manuscripts of papers for publication in the Society's Journal are to be found in the "Guide to Authors," which is obtainable on application to the Honorary Secretaries of the Society.

 FORM OF BEQUEST.

I bequeath the sum of £ to the ROYAL SOCIETY OF NEW SOUTH WALES, Incorporated by Act of the Parliament of New South Wales in 1881, and I declare that the receipt of the Treasurer for the time being of the said Corporation shall be an effectual discharge for the said Bequest, which I direct to be paid within calendar months after my decease, without any reduction whatsoever, whether on account of Legacy Duty thereon or otherwise, out of such part of my estate as may be lawfully applied for that purpose.

[Those persons who feel disposed to benefit the Royal Society of New South Wales by Legacies, are recommended to instruct their Solicitors to adopt the above Form of Bequest.]

The following publications of the Society, if in print, can be obtained at the Society's Rooms, Science House, Gloucester and Essex Streets, Sydney.

Transactions of the Philosophical Society, N.S.W., 1862-5, pp. 374, out of print.					
Vols.	I-XI Transactions of the Royal Society, N.S.W., 1867-1877				
Vol.	XII	Journal and Proceedings			
					1878, pp. 324, price 10s. 6d.
"	XIII	"	"	"	1879, " 255, "
"	XIV	"	"	"	1880, " 391, "
"	XV	"	"	"	1881, " 440, "
"	XVI	"	"	"	1882, " 327, "
"	XVII	"	"	"	1883, " 324, "
"	XVIII	"	"	"	1884, " 224, "
"	XIX	"	"	"	1885, " 240, "
"	XX	"	"	"	1886, " 396, "
"	XXI	"	"	"	1887, " 296, "
"	XXII	"	"	"	1888, " 390, "
"	XXIII	"	"	"	1889, " 534, "
"	XXIV	"	"	"	1890, " 290, "
"	XXV	"	"	"	1891, " 348, "
"	XXVI	"	"	"	1892, " 426, "
"	XXVII	"	"	"	1893, " 530, "
"	XXVIII	"	"	"	1894, " 368, "
"	XXIX	"	"	"	1895, " 600, "
"	XXX	"	"	"	1896, " 568, "
"	XXXI	"	"	"	1897, " 626, "
"	XXXII	"	"	"	1898, " 476, "
"	XXXIII	"	"	"	1899, " 400, "
"	XXXIV	"	"	"	1900, " 484, "
"	XXXV	"	"	"	1901, " 581, "
"	XXXVI	"	"	"	1902, " 531, "
"	XXXVII	"	"	"	1903, " 663, "
"	XXXVIII	"	"	"	1904, " 604, "
"	XXXIX	"	"	"	1905, " 274, "
"	XL	"	"	"	1906, " 368, "
"	XLI	"	"	"	1907, " 377, "
"	XLII	"	"	"	1908, " 593, "
"	XLIII	"	"	"	1909, " 466, "
"	XLIV	"	"	"	1910, " 719, "
"	XLV	"	"	"	1911, " 611, "
"	XLVI	"	"	"	1912, " 275, "
"	XLVII	"	"	"	1913, " 318, "
"	XLVIII	"	"	"	1914, " 584, "
"	XLIX	"	"	"	1915, " 587, "
"	L	"	"	"	1916, " 362, "
"	LI	"	"	"	1917, " 786, "
"	LII	"	"	"	1918, " 624, "
"	LIII	"	"	"	1919, " 414, "
"	LIV	"	"	"	1920, " 312, price £1 1s.
"	LV	"	"	"	1921, " 418, "
"	LVI	"	"	"	1922, " 372, "
"	LVII	"	"	"	1923, " 421, "
"	LVIII	"	"	"	1924, " 366, "
"	LIX	"	"	"	1925, " 468, "
"	LX	"	"	"	1926, " 470, "
"	LXI	"	"	"	1927, " 492, "
"	LXII	"	"	"	1928, " 458, "
"	LXIII	"	"	"	1929, " 263, "
"	LXIV	"	"	"	1930, " 434, "
"	LXV	"	"	"	1931, " 366, "
"	LXVI	"	"	"	1932, " 601, "
"	LXVII	"	"	"	1933, " 511, "
"	LXVIII	"	"	"	1934, " 328, "
"	LXIX	"	"	"	1935, " 288, "
"	LXX	"	"	"	1936, " 528, "
"	LXXI	"	"	"	1937, " 708, "
"	LXXII	"	"	"	1938, " 396, "
"	LXXIII	"	"	"	1939, " 344, "
"	LXXIV	"	"	"	1940, " 658, "
"	LXXV	"	"	"	1941, " 224, "
"	LXXVI	"	"	"	1942, " 432, "
"	LXXVII	"	"	"	1943, " 222, "
"	LXXVIII	"	"	"	1944, " 388, "

Royal Society of New South Wales

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W. H. MAZE, M.Sc.
F. R. MORRISON, A.A.C.I., F.C.S.
R. S. NYHOLM, M.Sc.
H. H. THORNE, M.A., B.Sc., F.R.A.S.
H. W. WOOD, M.Sc., A.Inst.P., F.R.A.S.

LIST OF THE MEMBERS
OF THE
Royal Society of New South Wales
as at March 1, 1945

P Members who have contributed papers which have been published in the Society's Journal. The numerals indicate the number of such contributions.

† Life Members.

Elected.

1944		Adamson, Colin Lachlan, Chemist, 22 Cremorne-street, Richmond, Vic.
1938	P 2	† Albert, Adrien, Ph.D. <i>Lond.</i> , B.Sc. <i>Syd.</i> , A.R.I.C. <i>Gt. B.</i> , Commonwealth Research Fellow in Organic Chemistry, University of Sydney; p.r. "Greenknowe," Greenknowe-avenue, Potts Point.
1935		† Albert, Michel Francois, "Boomerang," Billyard-avenue, Elizabeth Bay.
1898		† Alexander, Frank Lee, Surveyor, 67 Ocean-street, Woollahra.
1941		† Alldis, Victor le Roy, L.S., Registered Surveyor, Young, N.S.W.
1909	P 12	† Andrews, Ernest C., B.A., Hon. Mem. Washington Academy of Sciences and of Royal Society of New Zealand, No. 4, "Kuring-gai," 241 Old South Head-road, Bondi. (President, 1921.)
1930		Aston, Ronald Leslie, B.Sc., B.E. <i>Syd.</i> , M.Sc., Ph.D. <i>Cantab.</i> , A.M.I.E.Aust., Lecturer in Civil Engineering and Surveying in the University of Sydney; p.r. 24 Redmyre-road, Strathfield.
1919	P 1	Arousseau, Marcel, B.Sc., 16 Woodland-street, Balgowlah.
1935		Back, Catherine Dorothy Jean, M.Sc., The Women's College, Newtown.
1924	P 1	Bailey, Victor Albert, M.A., D.Phil., F.Inst.P., Professor of Experimental Physics in the University of Sydney.
1934	P 1	Baker, Stanley Charles, M.Sc., A.Inst.P., Head Teacher of Physics, Newcastle Technical College, Tighe's Hill; p.r. 8 Hewison-street, Tighe's Hill, N.S.W.
1937		Baldick, Kenric James, B.Sc., 19 Beaconsfield-parade, Lindfield.
1919		Bardsley, John Ralph, 76 Wright's-road, Drummoyne.
1939	P 2	Basnett, Elizabeth Marie, M.Sc., 36 Cambridge-street, Epping.
1933		Bedwell, Arthur Johnson, Eucalyptus Oil Merchant, "Kama," 10 Darling Point-road, Edgecliff.
1944		Bennett, Alwynne Drysdale, B.Sc., 8 Courland-street, Randwick.
1926		Bentivoglio, Sydney Ernest, B.Sc.Agr., Rosebery-road, Killara.
1940		Betty, Robert Cecil, 67 Imperial-avenue, Bondi.
1937	P 6	Birch, Arthur John, M.Sc., D.Phil. (<i>Oxon.</i>), 37 Museum-road, Oxford, England.
1923		Birks, George Frederick, Wholesale Druggist, c/o Potter & Birks Ltd., 15 Grosvenor-street, Sydney; p.r. 42 Powell-street, Killara.
1916		Birrell, Septimus, 74 Edinburgh-road, Marrickville.
1920		Bishop, Eldred George, Manufacturing and General Engineer, 37-45 Myrtle-street, Chippendale; p.r. 17 Thompson-street, Clifton Gardens.
1938	P 1	Black, Una Annie Frazer (Mrs.), B.Sc., Flat 2, 4 Clowes-street, South Yarra, Melbourne, Victoria.
1939	P 3	Blake, George Gascoigne, M.I.E.E., F.Inst.P., "Holmleigh," Cecil-avenue, Pennant Hills.
1933	P 24	Bolliger, Adolph, Ph.D., Director of Research, Gordon Craig Urological Research Laboratory, Department of Surgery, University of Sydney.
1920	P 9	Booth, Edgar Harold, M.C., D.Sc., F.Inst.P., New England University College, Armidale. (President, 1935.)
1939	P 3	Bosworth, Richard Charles Leslie, M.Sc., D.Sc. <i>Adel.</i> , Ph.D. <i>Camb.</i> , F.A.C.I., F.Inst.P., c/o C.S.R. Co., Pyrmont; p.r. 41 Spencer-road, Killara.
1938		Breckenridge, Marion, B.Sc., Department of Geology, University of Sydney; p.r. 19 Handley-avenue, Thornleigh.
1940		Bridgen, Alan Charles, B.Sc., 22 Kelso-street, Enfield.

Elected.

1919	P 1	Briggs, George Henry, D.Sc., Ph.D., F.Inst.P., Officer-in-Charge, Section of Physics, National Standards Laboratory of Australia, University Grounds, Sydney; p.r. 13 Findlay-avenue, Roseville.
1942		Brown, Desmond J., B.Sc., 9 Agnes-street, Strathfield.
1935	P 4	Brown, Ida Alison, D.Sc., Lecturer in Palaeontology, University of Sydney.
1941		Brown, Samuel Raymond, A.C.A. Aust., 87 Ashley-street, Chatswood.
1913	P 22	Browne, William Rowan, D.Sc., Reader in Geology in the University of Sydney. (President, 1932.)
1940		Buckley, Daphne M. (Mrs.), B.Sc., 29 Abingdon-road, Roseville.
1940		Buckley, Lindsay Arthur, B.Sc., 29 Abingdon-road, Roseville.
1943		Burfitt, Barbara Joyce, M.B., B.S., Captain, A.I.F., 110 Elizabeth Bay-road, Elizabeth Bay, N.S.W.
1898		†Burfitt, W. Fitzmaurice, B.A., M.B., Ch.M., B.Sc. Syd., F.R.A.C.S., "Radstoke," Elizabeth Bay.
1926		Burkitt, Arthur Neville St. George, M.B., B.Sc., Professor of Anatomy in the University of Sydney.
1943		Burkitt, John Stanton, "Moonbi," 17 Cavell-street, West Hobart, Tas.
1940	P 1	Cane, Reginald Frank, M.Sc., A.A.C.I., General Motors-Holdens Ltd., Fishermen's Bend, Melbourne, Victoria; p.r. 2 David-street, St. Kilda, S.2.
1940		Callanan, Victor John, B.Sc., 17 Wheatleigh-street, Naremburn.
1938	P 2	†Carey, Samuel Warren, D.Sc., Government Geologist, Department of Mines, Hobart, Tasmania.
1903	P 5	†Carslaw, Horatio Scott, Sc.D., LL.D., F.R.S.E., Emeritus Professor of Mathematics, University of Sydney, Fellow of Emmanuel College, Cambridge; Burradoo, N.S.W.
1944		Cavill, George William Kenneth, B.Sc., Department of Chemistry, Technical College, Harris-street, Ultimo; p.r. 40 Chandos-street, Ashfield.
1913	P 4	Challinor, Richard Westman, F.R.I.C., A.A.C.I., A.S.T.C., F.C.S.; p.r. 54 Drumalbyn-road, Bellevue Hill. (President, 1933.)
1933		Chalmers, Robert Oliver, A.S.T.C., Scientific Liaison Bureau, Box 4061, G.P.O., Sydney.
1940		Chambers, Maxwell Clark, B.Sc., c/o J. and E. Atkinson Pty. Ltd., 469-75 Kent-street, Sydney.
1913	P 21	Cheel, Edwin, 40 Queen-street, Ashfield. (President, 1931.)
1935	P 2	Churchward, John Gordon, B.Sc.Agr., Ph.D., 1 Hunter-street, Woolwich.
1935		Clark, Sir Reginald Marcus, K.B.E., Central Square, Sydney.
1940		Clarke, Ronald Stuart, B.A., 28 Beecroft-road, Beecroft.
1938		Clune, Francis Patrick, Author and Accountant, 15 Prince's-avenue, Vaucluse.
1941		Cohen, Max Charles, B.Sc., A.I.F., 80 "St. James," Stanley-street, Sydney.
1940		Cohen, Samuel Bernard, M.Sc., A.A.C.I., 34 Euroka-street, Northbridge.
1940	P 1	Colditz, Margaret Joyce, B.Sc., 9 Beach-street, Kogarah.
1940		Cole, Edward Ritchie, B.Sc., 14 Barwon-road, Lane Cove.
1940	P 1	Cole, Joyce Marie, B.Sc., 14 Barwon-road, Lane Cove.
1940		Collett, Gordon, B.Sc., 20 Duchess-avenue, Fivedock.
1920		Cooke, Frederick, c/o Meggitt's Limited, Asbestos House, York and Barrack-streets, Sydney.
1913	P 5	Coombs, F. A., F.C.S., Instructor of Leather Dressing and Tanning, Sydney Technical College; p.r. Bannerman-crescent, Rosebery.
1933		Corbett, Robert Lorimer, Managing Director of Robert Corbett & Co. Ltd., Manufacturing Chemists, Head Office, 379 Kent-street, Sydney.
1937	P 8	Cornforth, Rita Harriet, D.Phil. (Oxon.), M.Sc. (Syd.), c/o Dyson Perrin's Laboratory, South Parks-road, Oxford, England.
1940		Cortis-Jones, Beverly, M.Sc., 62 William-street, Roseville.
1919		Cotton, Frank Stanley, D.Sc., Research Professor in Physiology in the University of Sydney.
1909	P 7	†Cotton, Leo Arthur, M.A., D.Sc., Professor of Geology in the University of Sydney. (President, 1929.)
1941	P 3	Craig, David Parker, Research Scholar, 62 Springdale-road, Killara.
1921	P 1	†Cresswick, John Arthur, A.A.C.I., F.C.S., Production Superintendent and Chief Chemist, c/o The Metropolitan Meat Industry Commissioner, State Abattoir and Meat Works, Homebush Bay; p.r. 101 Villiers-street, Rockdale.
1940	P 4	Crockford, Joan Marian, B.Sc., 219 Victoria-road, Gladesville.
1935	P 3	Culey, Alma Gertrude, M.Sc., 37 Neirbo-avenue, Hurstville.
1940		Dadour, Anthony, B.Sc., 25 Elizabeth-street, Waterloo.
1890		†Dare, Henry Harvey, M.E., M.Inst.C.E., M.I.E.Aust., 14 Victoria-street, Roseville.
1919	P 2	de Beuzeville, Wilfred Alex. Watt, J.P., "Mélamere," Welham-street, Beecroft.

Elected.

- 1908 †Dixson, William, "Merridong," Gordon-road, Killara.
 1913 P 3 Doherty, William M., F.R.I.C., F.A.C.I., 36 George-street, Marrickville.
 1928 Donegan, Henry Arthur James, A.S.T.C., A.A.C.I., Analyst, Department of Mines, Sydney; p.r. 18 Hillview-street, Sans Souci.
 1943 Dudgeon, William, Manager, Commonwealth Drug Co., 50-54 Kippax-street, Sydney.
 1937 P 7 Dulhunty, John Allan, B.Sc., Geology Department, University of Sydney.
 1924 Dupain, George Zephirin, A.A.C.I., F.C.S., Director Dupain Institute of Physical Education and Medical Gymnastics, Manning Building, 449 Pitt-street, Sydney; p.r. "Rose Bank," 158 Parramatta-road, Ashfield.
 1934 P 25 Dwyer, Francis P. J., M.Sc., Lecturer in Chemistry, Technical College, Sydney.
 1923 P 21 Earl, John Campbell, D.Sc., Ph.D., Professor of Organic Chemistry in the University of Sydney. (President, 1938.)
 1924 Eastaugh, Frederick Alldis, A.R.S.M., F.R.I.C., Professor in Engineering Technology and Metallurgy in the University of Sydney.
 1934 P 2 Elkin, Adolphus Peter, M.A., Ph.D., Professor of Anthropology in the University of Sydney. (President, 1940. Hon. Secretary.)
 1940 Emmerton, Henry James, B.Sc., 41 Nelson-street, Gordon.
 1937 English, James Roland, L.S. A.I.F.
 1916 P 2 Enright, Walter John, B.A., Solicitor, High-street, West Maitland; p.r. Regent-street, West Maitland.
 1944 Erhart, John Charles, Chemical Engineer, 33 Beaconsfield-parade, Lindfield.
 1908 †Esdaile, Edward William, 42 Hunter-street, Sydney.
 1935 Evans, Silvanus Gladstone, A.I.A.A. Lond., A.R.A.I.A., 6 Major-street, Coogee.
 1921 Farnsworth, Henry Gordon, "Rothsay," 90 Alt-street, Ashfield.
 1939 Faull, Norman Augustus, B.Sc., A.Inst.P., c/o National Standards Laboratory, University Grounds, City-road, Chippendale.
 1909 P 7 †Fawsitt, Charles Edward, D.Sc., Ph.D., F.A.C.I., Professor of Chemistry in the University of Sydney. (President, 1919.)
 1940 Finch, Franklin Charles, B.Sc., Kirby-street, Rydalmere, N.S.W.
 1927 P 7 Finnermore, Horace, B.Sc., F.R.I.C., Reader in Pharmacy in the University of Sydney.
 1940 Fisher, Robert, B.Sc., 3 Sackville-street, Maroubra.
 1920 Fisk, Sir Ernest Thomas, K.B., F.Inst.R.E., A.M.I.E. Aust., Managing Director, Electric and Musical Industries Ltd., Blyth-road, Hayes, Middlesex, England.
 1940 Flack, Arthur Charles Allenby, B.Sc., Agricultural High School, Yanco, N.S.W.
 1933 Fletcher, Harold Oswald, Assistant Palaeontologist, Australian Museum, College-street, Sydney.
 1879 †Foreman, Joseph, M.R.C.S. Eng., L.R.C.P. Edin., "The Astor," Macquarie-street, Sydney.
 1932 Forman, Kenn. P., M.I.Refr.E., c/o Department of Aircraft Production, Box 20935, Melbourne, Vic.
 1905 †Foy, Mark, c/o Geo. O. Bennett, 133 Pitt-street, Sydney.
 1940 Franki, Robert James Anning, B.Sc., 891 New South Head-road, Rose Bay.
 1943 Frederick, Robert Desider Louis, B.E., 6 "Trinity Court," Telopea-street, Wollstonecraft.
 1940 Freney, Martin Raphael, B.Sc., Central Wool Testing House, 17 Randle-street, Sydney.
 1944 Friend, James Alan, 16 Kelburn-road, Roseville.
 1935 P 2 Garretty, Michael Duhan, M.Sc., Chief Geologist, North Broken Hill Ltd., Broken Hill, N.S.W.
 1939 P 2 Gascoigne, Robert Mortimer, 5 Werona-avenue, Killara.
 1926 Gibson, Alexander James, M.E., M.Inst.C.E., M.I.E.Aust., Consulting Engineer, 906 Culwulla Chambers, 67 Castlereagh-street, Sydney; p.r. "Wirruna," Belmore-avenue, Wollstonecraft.
 1942 P 2 Gibson, Neville Allan, B.Sc., Industrial Chemist, 217 Parramatta-road, Haberfield.
 1940 Gillis, Richard Galvin, 1 Dundee, 35 Adams-street, South Yarra, S.E.1, Vic.
 1935 Goddard, Roy Hamilton, F.C.A. Aust., Royal Exchange, Bridge-street, Sydney.
 1936 Goulston, Edna Maude, B.Sc., Third Officer, W.R.A.N.S., Navy Office, Melbourne.

Elected.

- 1940 Graves, John Nevil, B.Sc., 96 Wentworth-street, Randwick.
 1938 Griffiths, Edward L., B.Sc., A.A.C.I., A.B.I.C., Chief Chemist, Department of Agriculture; p.r. 151 Wollongong-road, Arncliffe.
- 1934 Hall, Norman Frederick Blake, M.Sc., Chemist, Council for Scientific and Industrial Research (Tobacco Section), Dept. of Organic Chemistry, University of Sydney; p.r. 15A Wharf-road, Longueville.
- 1892 †Halloran, Henry Ferdinand, L.S., A.M.I.E.Aust., F.S.I.Eng., M.T.P.I.Eng., 153 Elizabeth-street, Sydney; p.r. 23 March-street, Bellevue Hill.
- 1940 P 2 Hanlon, Frederick Noel, B.Sc., Geologist, Department of Mines, Sydney; p.r. 12 Countess-street, Mosman.
- 1905 P 6 †Harker, George, D.Sc., F.A.C.I.; p.r. 89 Homebush-road, Strathfield.
- 1936 Harper, Arthur Frederick Alan, M.Sc., A.Inst.P., National Standards Laboratory, University Grounds, City-road, Chippendale.
- 1934 Harrington, Herbert Richard, Teacher of Physics and Electrical Engineering, Technical College, Harris-street, Ultimo.
- 1929 Hawley, J. William, J.P., Financial Agent, 4 Castlereagh-street, Sydney; p.r. 12 King's-road, Vauluse.
- 1934 Hayes, William Lyall, A.S.T.C., A.A.C.I., Works Chemist, c/o Messrs. Wm. Cooper & Nephews (Aust.) Ltd., Phillip-street, Concord; p.r. 101 Essex-street, Epping.
- 1919 Henriques, Frederick Lester, 208 Clarence-street, Sydney.
- 1938 P 4 Hill, Dorothy, M.Sc. Q'ld., Ph.D. Cantab., Geological Research Fellow, University of Queensland, Brisbane.
- 1918 Hindmarsh, Percival, M.A. B.Sc.Agr., Principal, Hurlstone Agricultural High School, Glenfield.
- 1936 Hirst, Edward Eugene, A.M.I.E., Vice-Chairman and Joint Managing Director, British General Electric Co. Ltd.; p.r. "Springmead," Ingleburn.
- 1928 Hirst, George Walter Cansdell, B.Sc., A.M.I.E. (Aust.), "St. Cloud," Beaconsfield-road, Chatswood.
- 1916 Hoggan, Henry James, A.M.I.M.E. Lond., A.M.I.E. Aust., Consulting and Designing Engineer, N.R.M.A. House, 3 Spring-street, Sydney.
- 1941 Howard, Harold Theodore Clyde, B.Sc., Principal, Wollongong Technical High School, Wollongong.
- 1935 Howarth, Mark, F.R.A.S., Grange Mount Observatory, Bull-street, Mayfield, Newcastle, N.S.W.
- 1938 P 4 Hughes, Gordon Kingsley, B.Sc., Lecturer in Chemistry, University of Sydney.
- 1923 P 3 †Hynes, Harold John, D.Sc., B.Sc.Agr., Biologist, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. "Belbooree," 10 Wandella-avenue, Roseville.
- 1943 Iredale, Thomas, B.Sc., D.Sc., F.R.I.C., Chemistry Department, University of Sydney; p.r. 96 Roseville-avenue, Roseville.
- 1942 P 1 Jaeger, John Conrad, M.A., D.Sc., University of Tasmania, Hobart, Tasmania.
- 1940 Johns, Thomas Harley, 130 Smith-street, Summer Hill.
- 1909 P 15 Johnston, Thomas Harvey, M.A., D.Sc., C.M.Z.S., Professor of Zoology in the University of Adelaide. (Cor. Mem., 1912.)
- 1935 P 6 Joplin, Germaine Anne, B.Sc., Ph.D., Geological Department, University of Sydney; p.r. 18 Wentworth-street, Eastwood.
- 1930 Judd, William Percy, 123 Wollongong-road, Arncliffe.
- 1911 Julius, Sir George A., Kt., B.Sc., B.E., M.I.Mech.E., M.I.E.Aust., Culwulla Chambers, Castlereagh-street, Sydney.
- 1935 Kelly, Caroline Tennant (Mrs.), "Eight Bells," Castle Hill.
- 1940 Kennard, William Walter, 9 Bona Vista-avenue, Maroubra.
- 1924 P 1 Kenny, Edward Joseph, Geological Surveyor, Department of Mines, Sydney; p.r. 17 Alma-street, Ashfield.
- 1943 Kimble, Jean Annie, Research Chemist, B.Sc., 383 Marrickville-road, Marrickville.
- 1920 Kirchner, William John, B.Sc., A.A.C.I., Manufacturing Chemist, c/o Messrs. Burroughs Wellcome & Co. (Australia) Ltd., Victoria-street, Waterloo; p.r. 18 Lyne-road, Cheltenham.

Elected.

1939		Lambeth, Arthur James, B.Sc., "Naranje," Sweethaven-road, Wetherill Park, N.S.W.
1936		Leach, Stephen Laurence, B.A., B.Sc., A.A.C.I., Major, Scientific Liaison Officer, Victoria Barracks, Melbourne.
1920		Le Souef, Albert Sherbourne, 3 Silex-road, Mosman.
1929	P 55	†Lions, Francis, B.Sc., Ph.D., A.R.I.C., Department of Chemistry, University of Sydney.
1942		Lippmann, Arthur S., M.D., 175 Macquarie-street, Sydney.
1940	P 2	Lipson, Menzie, B.Sc., A.A.C.I., Chemist, C.S.I.R., Central Wool Committee Testing House, 17 Randle-street, Sydney.
1940	P 1	Lockwood, William Hutton, B.Sc., c.o. Department of Post-War Reconstruction, Hotel Acton, Canberra, A.C.T.
1906		†Loney, Charles Augustus Luxton, M.Am.Soc.Refr.E., National Mutual Building, 350 George-street, Sydney.
1943		Luber (Mrs.) Daphne, B.Sc., 98 Lang-road, Centennial Park.
1942		Lyons, Raymond Norman Matthew, M.Sc., Biochemical Research Worker, 8 Boronia-avenue, Wollstonecraft.
1939	P 3	Maccoll, Allan, M.Sc., Senior Lecturer in Chemistry, University of Sydney, Sydney.
1943		McCoy, William Kevin, Analytical Chemist, R.A.A.F.; p.r. 16 Bishop's-avenue, Randwick.
1940		McGrath, Brian James, 40 Mooramie-avenue, Kensington.
1940		McGregor, Gordon Howard, 4 Maple-avenue, Pennant Hills.
1906	P 2	†McIntosh, Arthur Marshall, "Moy Lodge," Hill-street, Roseville.
1891	P 1	†McKay, R. T., M.Inst.C.E., Eldon Chambers, 92 Pitt-street, Sydney.
1944	P 2	McKenzie, Hugh Albert, B.Sc., Assistant Research Officer, C.S.I.R.; p.r. 52 Bolton-street, Guildford.
1943		McKern, Howard Hamlet Gordon, A.S.T.C., A.A.C.I., Chemist, Meggitt Ltd., Parramatta; p.r. 14 Orwell-street, Potts Point.
1932		McKie, Rev. Ernest Norman, B.A. Syd., St. Columba's Manse, Guyra.
1927		McMaster, Sir Frederick Duncan, kt., "Dalkeith," Cassilis, N.S.W.
1940		Malone, Edward E., No. 4, Astral, 10 Albert-street, Randwick.
1924		Mance, Frederick Stapleton, "Binbah," Lucretia-avenue, Longueville.
1944		Martin, Cyril Maxwell, Chemist, 22 Wattle-street, Haberfield.
1935	P 1	Maze, Wilson Harold, M.Sc., Lecturer in Geography, University of Sydney.
1912		Meldrum, Henry John, B.A., B.Sc., Lecturer, The Teachers' College, University Grounds, Newtown; p.r. 98 Sydney-road, Manly.
1929	P 22	Mellor, David Paver, M.Sc., Lecturer, Chemistry Department, University of Sydney; p.r. 137 Middle Harbour-road, Lindfield. (President, 1941-42. Joint Hon. Secretary.)
1941		Melville, George Livingstone, Managing Director, Federal Machine Co. Ltd., Loftus-street, Arncliffe.
1940		Mercer, Edgar Howard, McMaster Laboratory, Parramatta-road, Glebe.
1928		Michell, Louis Ivan Allan, M.Sc., Ph.D., Research Chemist, c/o Colonial Sugar Refining Co., Pyrmont.
1940		Millership, William, M.Sc., Chief Chemist, Davis Gelatine (Aust.) Pty. Ltd., 15 Shaw-avenue, Earlwood.
1943		Molloy, Ernest Patrick, Assistant Sectional Manager, 129 Gibbes-street, Rockdale.
1941		Morrissey, Matthew John, B.A., A.S.T.C., Auburn-street, Parramatta.
1922	P 27	Morrison, Frank Richard, A.A.C.I., F.C.S., Assistant Chemist, Technological Museum, Sydney.
1934		Mort, Francis George Arnot, A.A.C.I., Chemist, 16 Grafton-street, Woollahra.
1944		Moye, Daniel George, Chemist, "Whiporie," Holland-street, Cronulla.
1915		Murphy, Robert Kenneth, Dr.Ing., Chem.Eng., A.S.T.C., M.I.Chem.E., F.A.C.I., Lecturer in Charge of Chemistry and Head of Science Department, Sydney Technical College.
1923	P 2	Murray, Jack Keith, QX34748, B.A., B.Sc.Agr., c/o H.Q., Angau, New Guinea Force, and Professor of Agriculture in the University of Queensland.
1930	P 6	Naylor, George Francis King, M.A., M.Sc., Dip.Ed., A.A.I.I.P., Squadron Leader, R.A.A.F., Headquarters, Melbourne; p.r. "Kingsleigh," Ingleburn, N.S.W.

Elected.

1943		Neuhaus, John William George, c/o Meggitt Ltd., Parramatta.
1932		Newman, Ivor Vickery, M.Sc., Ph.D., F.R.M.S., F.L.S., Department of Biology, Victoria University College, Wellington, N.Z.
1943		Nicol, Alexander Campbell, A.S.T.C., A.A.C.I., Chief Chemist, Crown Crystal Glass Co.; p.r. No. 12 "Florida," 519 New South Head-road, Double Bay.
1938	P 1	Noble, Norman Scott, D.Sc.Agr., M.Sc., D.I.C., Secretary, Linnean Society of N.S.W., Science House, Gloucester-street, Sydney.
1920	P 4	†Noble, Robert Jackson, M.Sc., B.Sc.Agr., Ph.D., Under Secretary, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. 32A Middle Harbour-road, Lindfield. (President, 1934.)
1940		Norrie, Jack Campbell, B.Sc., 28 Ray-road, Epping.
1940	P 13	Nyholm, Ronald Sydney, M.Sc., 77 Bland-street, Ashfield.
1935		O'Connell, Rev. Daniel J. K., S.J., M.Sc., F.R.A.S., Riverview College Observatory, Sydney.
1903		†Old, Richard, "Waverton," Bay-road, North Sydney.
1921	P 5	Osborne, George Davenport, D.Sc. Syd., Ph.D. Camb., Lecturer and Demonstrator in Geology in the University of Sydney.
1920	P 74	Penfold, Arthur Ramon, F.A.C.I., F.C.S., Curator and Economic Chemist, Technological Museum, Harris-street, Ultimo; p.r. 67 Park-avenue, Roseville. (President, 1935.)
1938		Phillips, Marie Elizabeth, B.Sc., 4 Morella-road, Clifton Gardens.
1935		Phillips, Orwell, 55 Darling Point-road, Edgecliffe.
1943		Plowman, Ronald Arthur, A.S.T.C., A.A.C.I., Analytical Chemist, 78 Alt-street, Ashfield.
1919		Poate, Hugh Raymond Guy, M.B., Ch.M. Syd., F.R.C.S. Eng., L.R.C.P. Lond., F.R.A.C.S., Surgeon, 225 Macquarie-street, Sydney; p.r. 38 Victoria-road, Bellovue Hill.
1896		†Pope, Roland James, B.A. Syd., M.D., Ch.M., F.R.C.S. Ind., 185 Macquarie-street, Sydney.
1921	P 2	Powell, Charles Wilfrid Roberts, F.R.I.C., A.A.C.I., Company Executive, c/o Colonial Sugar Refining Co., O'Connell-street, Sydney; p.r. "Wansfell," Kirkoswald-avenue, Mosman.
1918		Powell, John, Director, Foster Clark (Aust.) Ltd., 17 Thurlow-street, Redfern; p.r. "Elgarth," Ranger's-road, Cremorne.
1938		Powell, John Wallis, A.S.T.C., A.A.C.I., Managing Director, Foster Clark (Aust.) Ltd., 17 Thurlow-street, Redfern.
1927		Price, William Lindsay, B.E., B.Sc., Teacher of Physics, Sydney Technical College; p.r. 8 Wattle-street, Killara.
1918	P 1	Priestley, Henry, M.D., Ch.M., B.Sc., Professor of Biochemistry, Faculty of Medicine, the University of Sydney. (President, 1942-43.)
1893		†Purser, Cecil, B.A., M.B., Ch.M. Syd., "Ascot," Grosvenor-road, Wahroonga.
1935	P 3	†Quodling, Florrie Mabel, B.Sc., Demonstrator in Geology, University of Sydney.
1922	P 6	Raggatt, Harold George, D.Sc., Director, Mineral Resources Survey, Department of Supply, Canberra, A.C.T.
1940	P 1	Ralph, Colin Sydney, B.Sc., 24 Canberra-street, Epping.
1919	P 3	Randclaud, Archibald Boscawen Boyd, B.Sc., B.E., Lecturer in Physics, Teachers' College, The University, Sydney.
1936		Randall, Harry, Buena Vista-avenue, Denistone.
1931	P 1	Rayner, Jack Maxwell, B.Sc., F.Inst.P., Chief Geophysicist, Mineral Resources Survey, Department of Supply and Shipping, Census Building, Canberra, A.C.T.
1935		Reid, Cicero Augustus, 19 Newton-road, Strathfield.
1939	P 14	Ritchie, Ernest, B.Sc., 6 Military-road, North Bondi.
1933		Roberts, Richard George Crafter, Electrical Engineer, c/o C. W. Stirling & Co., Asbestos House, York and Barrack-streets, Sydney.
1940		Robertson, Rutherford Ness, B.Sc. Syd., Ph.D. Cantab., Flat 4, 43 Johnston-street, Annandale.
1935	P 2	Room, Thomas G., M.A., F.R.S., Professor of Mathematics in the University of Sydney.

Elected.		
1940		Rosenbaum, Sidney, 44 Gilderthorp-avenue, Randwick.
1928		Ross, Allan Clunies, B.Sc., F.C.A. <i>Aust.</i> , Chartered Accountant <i>Aust.</i> , 54A Pitt-street, Sydney; p.r. The Grove, Woollahra. (Member from 1915 to 1924.) (Hon. Treasurer.)
1940		Ross, Jean Elizabeth, B.Sc., Dip.Ed., 5 Stanton-road, Haberfield.
1935		Savage, Clarence Golding, Director of Fruit Culture, Department of Agriculture, Sydney.
1941	P 2	Sawkins, Dansie Thomas, M.A. <i>Syd.</i> , B.A. <i>Camb.</i> , Reader in Statistics, The University, Sydney; p.r. 60 Boundary-street, Roseville.
1920		Scammell, Rupert Boswood, B.Sc. <i>Syd.</i> , A.A.C.I., F.C.S., c/o F. H. Faulding & Co. Ltd., 98 Castlereagh-street, Redfern; p.r. 10 Buena Vista-avenue, Clifton Gardens.
1940		Scott, Reginald Henry, B.Sc., 3 Walbundry-avenue, East Kew, Victoria.
1933		Selby, Esmond Jacob, Dip.Com., Sales Manager, Box 175 D, G.P.O., Sydney.
1936		Sellenger, Brother Albertus, Marist Brothers' College, Randwick, N.S.W.
1938		Sheahan, Thomas Henry Kennody, B.Sc., Chemist, 2 Edward-street, Gordon.
1936	P 2	Sherrard, Kathleen Margaret Maria (Mrs.), M.Sc. <i>Melb.</i> , 43 Robertson-road, Centennial Park.
1917		Sibley, Samuel Edward, Mount-street, Coogee.
1900		†Simpson, R. C., Park-avenue, Roseville.
1943		Simpson, John Kenneth Moore, Industrial Chemist, "Browie," Old Castle Hill-road, Castle Hill.
1933		Slade, George Hermon, B.Sc., Director, W. Hermon Slade & Co. Pty. Ltd., Manufacturing Chemists, Mandemar-avenue, Homebush; p.r. "Raiaeta," Oyama-avenue, Manly.
1940		Smith, Eric Brian Jeffcoat, 1 Rocklands-road, Wollstonecraft.
1922	P 1	Smith, Thomas Hodge, Australian Museum, College-street, Sydney.
1919		Southee, Ethelbert Ambrook, O.B.E., M.A., B.Sc., B.Sc.Agr., Principal, Hawkesbury Agricultural College, Richmond, N.S.W.
1921		Spencer-Watts, Arthur, "Araboona," Glebe-street, Randwick.
1916		Stephen, Alfred Ernest, F.C.S., c/o Box 1158 HH, G.P.O., Sydney.
1914		Stephens, Frederick G. N., F.R.C.S., M.B., Ch.M., 135 Macquarie-street, Sydney; p.r. Captain Piper's-road and New South Head-road, Vaucluse.
1900	P 1	†Stewart, J. Douglas, B.V.Sc., F.R.C.V.S., Emeritus Professor of Veterinary Science in the University of Sydney; p.r. "Berelle," Homobush-road, Strathfield. (President, 1927.)
1942		Still, Jack Leslie, B.Sc., Ph.D., Department of Biochemistry, The University, Sydney.
1916	P 1	Stone, Walter George, F.S.T.C., F.A.C.I., Chief Analyst, Department of Mines, Sydney.
1940		Stroud, Richard Harris, B.Sc., "Dalveen," corner Chalmers and Barker-roads, Strathfield.
1918		†Sullivan, Herbert Jay, Director in Charge of Research and Technical Department, c/o Lewis Berger & Sons (Australia) Ltd., Rhodes; Box 23, P.O., Burwood; p.r. "Stonycroft," 10 Redmyre-road, Strathfield.
1901	P 16	†Susasmilch, C. A., F.G.S., F.S.T.C., Consulting Geologist, 11 Appian Way, Burwood. (President, 1922.)
1919		†Sutherland, George Fife, A.R.C.Sc. <i>Lond.</i> , Assistant Professor of Mechanical Engineering in the University of Sydney.
1920		Sutton, Harvey, O.B.E., M.D., D.P.H. <i>Melb.</i> , B.Sc. <i>Oxon.</i> , Professor of Preventive Medicine and Director, School of Public Health and Tropical Medicine, University of Sydney; p.r. "Lynton," 27 Kent-road, Rose Bay.
1941	P 2	Swanson, Thomas Baikie, M.Sc. <i>Adel.</i> , c/o Technical Service Department, Icianz, Box 1911, G.P.O., Melbourne, Victoria.
1915	P 3	Taylor, Brigadier Harold B., M.C., D.Sc., F.R.I.C., F.A.C.I., Second Government Analyst, Department of Public Health, 93 Macquarie-street, Sydney; p.r. 44 Kenneth-street, Longueville.
1944		Thomas, Andrew David, Flight-Lieutenant, R.A.A.F., M.Sc., A.Inst.P., 1 Valley-road, Lindfield.
1939		Thomas, Mrs. A. V. M., 1 Valley-road, Lindfield.
1919		Thorne, Harold Henry, M.A. <i>Cantab.</i> , B.Sc. <i>Syd.</i> , F.R.A.S., Lecturer in Mathematics in the University of Sydney; p.r. 55 Railway-crescent, Beecroft.
1935		Tommerup, Eric Christian, M.Sc., A.A.C.I., Queensland Agricultural College, Lawes, via Brisbane, Queensland.

Elected

- 1923 Toppin, Richmond Douglas, A.B.I.C., 51 Crystal-street, Petersham.
- 1940 Tow, Aubrey James, M.Sc., No. 5, "Werrington," Manion-avenue, Rose Bay.
- 1932 P 8 Trikojus, Victor Martin, B.Sc., D.Phil., Professor of Biochemistry, The University, Melbourne.
- 1943 Turner, Ivan Stewart, M.A., M.Sc., Ph.D., Lecturer in Mathematics, University of Sydney; p.r. 120 Awaba-street, Mosman.
- 1940 Vernon, James, Ph.D., A.A.C.I., Chief Chemist, Colonial Sugar Refining Co., 1 O'Connell-street, Sydney.
- 1921 Vicars, Robert, Marrickville Woollen Mills, Marrickville.
- 1935 Vickery, Joyce Winifred, M.Sc., Botanic Gardens, Sydney; p.r. 17 The Promenade, Cheltenham.
- 1933 P 5 Voisey, Alan Heywood, M.Sc., Lecturer in Geology and Geography, New England University College, Armidale.
- 1903 P 10 †Vonwiller, Oscar U., B.Sc., F.Inst.P., Professor of Physics in the University of Sydney. (President, 1930.)
- 1943 Walker, James Foote, Company Secretary, 11 Brucedale-avenue, Epping.
- 1919 P 2 Walkom, Arthur Bache, D.Sc., Director, Australian Museum, Sydney; p.r. 45 Nelson-road, Killara. (Member from 1910-1913. President, 1943-44.)
- 1913 P 5 Wardlaw, Hy. Sloane Halcro, D.Sc. Syd., F.A.C.I., Lecturer and Demonstrator in Biochemistry in the University of Sydney. (President, 1939.)
- 1944 Warner, Harry, A.S.T.C., Chemist, 15 Belmore-road, Penshurst.
- 1921 †Waterhouse, Gustavus Athol, D.Sc., B.E., F.R.E.S., F.R.Z.S., c.o. Australian Museum, College-street, Sydney.
- 1924 Waterhouse, Leslie Vickery, B.E. Syd., Mining Engineer, Shell House, Car-rington-street, Box 58 CC, G.P.O., Sydney; p.r. 4 Bertha-road, Neutral Bay.
- 1919 P 1 Waterhouse, Lionel Lawry, B.E. Syd., Lecturer and Demonstrator in Geology in the University of Sydney.
- 1919 P 6 Waterhouse, Walter L., M.C., D.Sc.Agr., D.I.C., F.L.S., Reader in Agriculture, University of Sydney; p.r. "Hazelmere," Chelmsford-avenue, Lindfield. (President, 1937.)
- 1944 Watkins, William Hamilton, B.Sc., Industrial Chemist, 57 Bellevue-street, North Sydney.
- 1941 P 1 Watson, Irvine Armstrong, Ph.D., B.Sc.Agr., Assistant Lecturer, Faculty of Agriculture, University of Sydney.
- 1911 P 1 Watt, Robert Dickie, M.A., B.Sc., Professor of Agriculture in the University of Sydney; p.r. 64 Wentworth-road, Vauchuse. (President, 1925.)
- 1936 Wearne, Harold Wallis, 22 Yarabah-avenue, Gordon.
- 1920 P 1 Wellish, Edward Montague, M.A., Associate-Professor of Applied Mathematics in the University of Sydney; p.r. 15 Belgium-avenue, Roseville.
- 1921 Wenholz, Harold, B.Sc.Agr., Director of Plant Breeding, Department of Agri-culture, Sydney.
- 1909 P 3 †White, Charles Josiah, B.Sc., Lecturer in Chemistry, Teachers' College, Uni-versity Grounds, Newtown.
- 1940 P 1 White, Douglas Elwood, M.Sc., D.Phil., University of Western Australia, Nedlands, W.A.
- 1943 Whiteman, Reginald John Nelson, M.B., Ch.M., F.R.A.C.S., 143 Macquarie-street, Sydney.
- 1928 Wiesener, Frederick Abbey, M.B., Ch.M., D.O.M.S., Ophthalmic Surgeon, 143 Macquarie-street, Sydney; p.r. Jersey-road, Strathfield.
- 1942 Williams, Gordon Roy, B.Sc., 45 Conder-street, Burwood.
- 1944 Willis, John Bryan, B.Sc., Demonstrator in Chemistry, University of Sydney; p.r. Flat 2, Russell Hall, 17 Mount-street, Coogee.
- 1943 Winch, Leonard, B.Sc., Chief Chemist, Fielder's General Products Ltd., P.O. Box 143, Tamworth, N.S.W.
- 1940 Wogan, Samuel James, Range-road, Sarina, North Queensland.
- 1936 P 2 Wood, Harley Weston, M.Sc., A.Inst.P., F.R.A.S., Assistant Astronomer, Sydney Observatory.
- 1906 P 12 †Woolnough, Walter George, D.Sc., F.G.S., 9 Lockerbie Court, East St. Kilda, Victoria. (President, 1926.)
- 1916 Wright, George, Company Director, c/o Hector Allen, Son & Morrison, 16 Barrack-street, Sydney; p.r. "Wanawong," Castle Hill, N.S.W.
- 1921 Yates, Guy Carrington, Seedsman, c/o Arthur Yates & Co. Ltd., 184 Sussex-street, Sydney; p.r. Boomerang-street, Turrumurra.

HONORARY MEMBERS.

*Limited to Twenty.***Elected.**

1914	Hill, James P., D.Sc., F.R.S., Professor of Zoology, University College, Gower-street, London, W.C.1, England.
1915	Maitland, Andrew Gibb, F.G.S., "Bon Accord," 28 Melville-terrace, South Perth, W.A.
1912	Martin, Sir Charles J., C.M.G., D.Sc., F.R.S., Roebuck House, Old Chesterton, Cambridge, England.
1922	Wilson, James T., M.B., Ch.M. <i>Edin.</i> , F.R.S., Professor of Anatomy in the University of Cambridge: p.r. 24 Millington-road, Cambridge, England.

OBITUARY, 1944-1945.

- 1905 Charles Anderson.
 1929 Norman Dawson Royle.
 1909 Edward Sutherland Stokes.
-

THE REV. W. B. CLARKE MEMORIAL FUND.

The Rev. W. B. Clarke Memorial Fund was inaugurated at a meeting of the Royal Society of N.S.W. in August, 1878, soon after the death of Mr. Clarke, who for nearly forty years rendered distinguished service to his adopted country, Australia, and to science in general. It was resolved to give an opportunity to the general public to express their appreciation of the character and services of the Rev. W. B. Clarke "as a learned colonist, a faithful minister of religion, and an eminent scientific man." It was proposed that the memorial should take the form of lectures on Geology (to be known as the Clarke Memorial Lectures), which were to be free to the public, and of a medal to be given from time to time for distinguished work in the Natural Sciences done in or on the Australian Commonwealth and its territories; the person to whom the award is made may be resident in the Australian Commonwealth or its territories, or elsewhere.

The Clarke Memorial Medal was established first, and later, as funds permitted, the Clarke Memorial Lectures have been given at intervals.

CLARKE MEMORIAL LECTURES.

Delivered.

1906. "The Volcanoes of Victoria," and "The Origin of Dolomite" (two lectures). By Professor E. W. Skeats, D.Sc., F.G.S.
1907. "Geography of Australia in the Permo-Carboniferous Period" (two lectures). By Professor T. W. E. David, B.A., F.R.S.
"The Geological Relations of Oceania." By W. G. Woolnough, D.Sc.
"Problems of the Artesian Water Supply of Australia." By E. F. Pittman, A.R.S.M.
"The Permo-Carboniferous Flora and Fauna and their Relations." By W. S. Dun.
1918. "Brain Growth, Education, and Social Inefficiency." By Professor R. J. A. Berry, M.D., F.R.S.E.
1919. "Geology at the Western Front." By Professor T. W. E. David, C.M.G., D.S.O., F.R.S.
1936. "The Aeroplane in the Service of Geology." By W. G. Woolnough, D.Sc. (THIS JOURN., 1936, 70, 39.)
1937. "Some Problems of the Great Barrier Reef." By Professor H. C. Richards, D.Sc. (THIS JOURN., 1937, 71, 68.)
1938. "The Simpson Desert and its Borders." By C. T. Madigan, M.A., B.Sc., B.E., D.Sc. (Oxon.). (THIS JOURN., 1938, 71, 503.)
1939. "Pioneers of British Geology." By Sir John S. Flett, K.B.E., D.Sc., LL.D., F.R.S. (THIS JOURN., 1939, 73, 41.)
1940. "The Geologist and Sub-surface Water." By E. J. Kenny, M.Aust.I.M.M. (THIS JOURN., 1940, 74, 283.)
1941. "The Climate of Australia in Past Ages." By C. A. Sussmilch, F.G.S. (THIS JOURN., 1941, 75, 47.)
1942. "The Heroic Period of Geological Work in Australia." By E. C. Andrews, B.Sc.
1943. "Australia's Mineral Industry in the Present War." By H. G. Raggatt, D.Sc.
1944. "An Australian Geologist Looks at the Pacific." By W. H. Bryan, M.C., D.Sc.

AWARDS OF THE CLARKE MEDAL.

Established in memory of

The Revd. WILLIAM BRANWHITE CLARKE, M.A., F.R.S., F.G.S., etc.

Vice-President from 1866 to 1878.

The prefix * indicates the decease of the recipient.

Awarded.

- 1878 *Professor Sir Richard Owen, K.C.B., F.R.S.
- 1879 *George Bentham, C.M.G., F.R.S.
- 1880 *Professor Thos. Huxley, F.R.S.
- 1881 *Professor F. M'Coy, F.R.S., F.G.S.
- 1882 *Professor James Dwight Dana, LL.D.
- 1883 *Baron Ferdinand von Mueller, K.C.M.G., M.D., Ph.D., F.R.S., F.L.S.
- 1884 *Alfred R. C. Selwyn, LL.D., F.R.S., F.G.S.
- 1885 *Sir Joseph Dalton Hooker, O.M., G.C.S.I., C.B., M.D., D.O.L., LL.D., F.R.S.
- 1886 *Professor L. G. De Koninck, M.D.

Awarded.

- 1887 *Sir James Hector, K.C.M.G., M.D., F.R.S.
- 1888 *Rev. Julian E. Tenison-Woods, F.G.S., F.L.S.
- 1889 *Robert Lewis John Ellery, F.R.S., F.R.A.S.
- 1890 *George Bennett, M.D., F.R.C.S. *Eng.*, F.L.S., F.Z.S.
- 1891 *Captain Frederick Wollaston Hutton, F.R.S., F.G.S.
- 1892 *Sir William Turner Thiselton Dyer, K.C.M.G., C.I.E., M.A., LL.D., Sc.D., F.R.S., F.L.S.
- 1893 *Professor Ralph Tate, F.L.S., F.G.S.
- 1895 *Robert Logan Jack, LL.D., F.G.S., F.R.G.S.
- 1895 *Robert Etheridge, Jnr.
- 1896 *The Hon. Augustus Charles Gregory, C.M.G., F.R.G.S.
- 1900 *Sir John Murray, K.C.B., LL.D., Sc.D., F.R.S.
- 1901 *Edward John Eyre.
- 1902 *F. Manson Bailey, C.M.G., F.L.S.
- 1903 *Alfred William Howitt, D.Sc., F.G.S.
- 1907 *Professor Walter Howchin, F.G.S., University of Adelaide.
- 1909 *Dr. Walter E. Roth, B.A.
- 1912 *W. H. Twelvetees, F.G.S.
- 1914 Sir A. Smith Woodward, LL.D., F.R.S., Keeper of Geology, British Museum (Natural History), London.
- 1915 *Professor W. A. Haswell, M.A., D.Sc., F.R.S.
- 1917 *Professor Sir Edgeworth David, K.B.E., C.M.G., D.S.O., M.A., Sc.D., D.Sc., F.R.S., F.G.S.
- 1918 *Leonard Rodway, C.M.G., Honorary Government Botanist, Hobart, Tasmania.
- 1920 *Joseph Edmund Carne, F.G.S.
- 1921 *Joseph James Fletcher, M.A., B.Sc.
- 1922 *Richard Thomas Baker, The Crescent, Cheltenham.
- 1923 *Sir W. Baldwin Spencer, K.C.M.G., M.A., D.Sc., F.R.S.
- 1924 *Joseph Henry Maiden, I.S.O., F.R.S., F.L.S., J.P.
- 1925 *Charles Hedley, F.L.S.
- 1927 Andrew Gibb Maitland, F.G.S., "Bon Accord," 28 Melville Terrace, South Perth, W.A.
- 1928 Ernest C. Andrews, B.A., F.G.S., 32 Benelong Crescent, Bellevue Hill.
- 1929 Professor Ernest Willington Skeats, D.Sc., A.R.C.S., F.G.S., University of Melbourne, Carlton, Victoria.
- 1930 L. Keith Ward, B.A., B.E., D.Sc., Government Geologist, Geological Survey Office, Adelaide.
- 1931 *Robin John Tillyard, M.A., D.Sc., Sc.D., F.R.S., F.L.S., F.E.S., Canberra, F.C.T.
- 1932 *Frederick Chapman, A.L.S., F.R.S.N.Z., F.G.S., Melbourne.
- 1933 Walter George Woolnough, D.Sc., F.G.S., Department of the Interior, Canberra, F.C.T.
- 1934 *Edward Sydney Simpson, D.Sc., B.E., F.A.C.I., Carlingford, Mill Point, South Perth, W.A.
- 1935 George William Card, A.R.S.M., 16 Ramsay-street, Collaroy, N.S.W.
- 1936 Sir Douglas Mawson, Kt., O.B.E., F.R.S., D.Sc., B.E., University of Adelaide
- 1937 J. T. Jutson, B.Sc., LL.B., 9 Ivanhoe-parade, Ivanhoe, Victoria.
- 1938 Professor H. C. Richards, D.Sc., The University of Queensland, Brisbane.
- 1939 C. A. Sussmilch, F.G.S., F.S.T.C., 11 Appian Way, Burwood, N.S.W.
- 1941 Professor Frederic Wood Jones, M.B., B.S., D.Sc., F.R.S., Anatomy Department, University of Manchester, England.
- 1942 William Rowan Browne, D.Sc., Reader in Geology, The University of Sydney, N.S.W.
- 1943 Walter Lawry Waterhouse, M.C., D.Sc.Agric., D.I.C., F.L.S., Reader in Agriculture, University of Sydney.
- 1944 Professor Wilfred Eade Agar, O.B.E., M.A., D.Sc., F.R.S., University of Melbourne, Carlton, Victoria.

AWARDS OF THE SOCIETY'S MEDAL AND MONEY PRIZE.

Money Prize of £25.

Awarded.

- 1882 John Fraser, B.A., West Maitland, for paper entitled "The Aborigines of New South Wales."
- 1882 Andrew Ross, M.D., Molong, for paper entitled "Influence of the Australian climate and pastures upon the growth of wool."

The Society's Bronze Medal and £25.

Awarded.

- 1884 W. E. Abbott, Wingen, for paper entitled "Water supply in the Interior of New South Wales."
- 1886 S. H. Cox, F.G.S., F.C.S., Sydney, for paper entitled "The Tin deposits of New South Wales."

Awarded.

- 1887 Jonathan Seaver, F.G.S., Sydney, for paper entitled "Origin and mode of occurrence of gold-bearing veins and of the associated Minerals."
- 1888 Rev. J. E. Tenison-Woods, F.G.S., F.L.S., Sydney, for paper entitled "The Anatomy and Life-history of Mollusca peculiar to Australia."
- 1889 Thomas Whitelegge, F.R.M.S., Sydney, for paper entitled "List of the Marine and Fresh-water Invertebrate Fauna of Port Jackson and Neighbourhood."
- 1889 Rev. John Mathew, M.A., Coburg, Victoria, for paper entitled "The Australian Aborigines."
- 1891 Rev. J. Milne Curran, F.G.S., Sydney, for paper entitled "The Microscopic Structure of Australian Rocks."
- 1892 Alexander G. Hamilton, Public School, Mount Kembla, for paper entitled "The effect which settlement in Australia has produced upon Indigenous Vegetation."
- 1894 J. V. De Coque, Sydney, for paper entitled the "Timbers of New South Wales."
- 1894 H. H. Mathews, L.S., Parramatta, for paper entitled "The Aboriginal Rock Carvings and Paintings in New South Wales."
- 1895 C. J. Martin, D.Sc., M.B., F.R.S., Sydney, for paper entitled "The physiological action of the venom of the Australian black snake (*Pseudechis porphyriacus*)."
- 1896 Rev. J. Milne Curran, Sydney, for paper entitled "The occurrence of Precious Stones in New South Wales, with a description of the Deposits in which they are found."
- 1943 Edwin Cheel, Sydney, in recognition of his contributions in the field of botanical research and to the advancement of science in general.

AWARDS OF THE WALTER BURFITT PRIZE.

Bronze Medal and Money Prize of £50.

Established as the result of a generous gift to the Society by Dr. W. F. BURFITT, B.A., M.B., Ch.M., B.Sc., of Sydney. Awarded at intervals of three years to the worker in pure and applied science, resident in Australia or New Zealand, whose papers and other contributions published during the past three years are deemed of the highest scientific merit, account being taken only of investigations described for the first time, and carried out by the author mainly in these Dominions.

Awarded.

- 1929 Norman Dawson Royle, M.D., Ch.M., 185 Macquarie Street, Sydney.
- 1932 Charles Halliboy Kellaway, M.C., M.D., M.S., F.R.C.P., The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.
- 1935 Victor Albert Bailey, M.A., D.Phil., Associate-Professor of Physics, University of Sydney.
- 1938 Frank Macfarlane Burnet, M.D. (Melb.), Ph.D. (Lond.), The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.
- 1941 Frederick William Whitehouse, D.Sc., Ph.D., University of Queensland, Brisbane.
- 1944 Hereward Leighton Kesteven, D.Sc., M.D., c/o Allied Works Council, Melbourne.

AWARDS OF LIVERSIDGE RESEARCH LECTURESHIP.

This Lectureship was established in accordance with the terms of a bequest to the Society by the late Professor Archibald Liversidge. Awarded at intervals of two years, for the purpose of encouragement of research in Chemistry. (THIS JOURNAL, Vol. LXII, pp. x-xiii, 1928.)

Awarded.

- 1931 Harry Hey, c/o The Electrolytic Zinc Company of Australasia, Ltd., Collins Street Melbourne.
- 1933 W. J. Young, D.Sc., M.Sc., University of Melbourne.
- 1940 G. J. Burrows, B.Sc., University of Sydney.
- 1942 J. S. Anderson, B.Sc., Ph.D. (Lond.), A.R.C.S., D.I.C., University of Melbourne.
- 1944 F. P. Bowden, Ph.D., Sc.D., University of Cambridge, Cambridge, England.

PRESIDENTIAL ADDRESS

By A. B. WALKOM, D.Sc.

Delivered to the Royal Society of New South Wales, April 5, 1944.

PART I. THE PAST YEAR.

In the fifth year of the second World War within the memory of most of us, our scientific societies are still able to carry on their activities. In this we are fortunate, for in many countries academic life and scientific research have been partly or completely disrupted. We should therefore take advantage of our favoured position not only to continue our normal activities as far as conditions permit, but to prepare ourselves to take part in post-war restoration in our own country and to assist in the rehabilitation of scientific activities in countries which have not been so fortunate.

Owing to the fact that more and more scientific workers are becoming absorbed in war-time activities, the number of research papers presented is smaller than usual, namely eighteen; the number of members of the Society shows a slight decrease and now stands at two hundred and eighty-seven.

The presentation of papers at monthly meetings during the year was supplemented by several talks and exhibits, some on recent scientific discoveries. The talks were:

“Penicillin and Gramicidin”, by Dr. F. Lions.

“Biotin”, by Professor H. Priestley.

“Reflection of Light from Film-covered Glass”, by Mr. J. Bannon.

“Evaporated Metal Films”, by Mr. F. P. J. Dwyer.

“The Future of the Native People of the South-west Pacific”, by Professor A. P. Elkin.

The Fluorescent Lamp—a new source of light—was the subject of an exhibit by Mr. D. P. Mellor.

As the lighting restrictions were relaxed during 1943, the Popular Science Lectures were resumed and on the whole were well attended.

Dr. H. G. Raggatt, formerly of the Geological Survey of New South Wales, and now Director of the Commonwealth Mineral Resources Survey, was invited to deliver the Clarke Memorial Lecture for 1943, and chose as his subject “Australia’s Mineral Industry in the Present War”.

Dr. W. L. Waterhouse was awarded the Clarke Memorial Medal for 1943 for his work in plant pathology and especially for his studies on varieties of wheat resistant to disease. For 1944, your Council has decided to award the Clarke Memorial Medal to Professor W. E. Agar, of the University of Melbourne.

The Society’s Medal was awarded to Mr. Edwin Cheel for his work on Australian botany and his contributions to the advancement of science.

Important events commemorated at meetings of the Society included the bi-centenary of the birth of Sir Joseph Banks, and the 400th anniversary of the publication by Copernicus of his work “De Revolutionibus Orbium Coelestium”, and the publication in the same year by Vesalius of “De Humani Corporis Fabrica”.

Our sister society the Royal Society of Tasmania celebrated its centenary in October, 1943, and a message of congratulation was sent by the Royal Society of New South Wales on this historic occasion.

We again acknowledge with thanks the grant from the Government of New South Wales of £400, which goes towards the publication of the Journal and Proceedings.

Consideration was given during the year to the further encouragement of research by the provision of research grants, and the Council decided to set aside a portion of our funds as a research fund, the interest on which may be used for this purpose.

Mr. Henry F. Halloran, who has been a member of the Society for more than fifty years, offered to donate funds for the institution of two medals, an offer which the Council gratefully accepted. One medal, to be known as the James Cook Medal, is to be awarded for scientific work in the southern hemisphere; the other, the Edgeworth David Medal, is for the encouragement of the younger members of the Society and will be awarded for outstanding research by members who have not attained the age of thirty-five years.

During the year, as your President, I attended several meetings of the Board of Visitors of the Sydney Observatory, and one meeting of the Donovan Trust. One of the meetings of the Board of Visitors was called specially to discuss the position of Government Astronomer, and I am pleased to be able to report that the recommendation made by the Board, that Mr. H. W. Wood, who had been Acting Government Astronomer, be appointed to the position, was followed in due course by the announcement that Mr. Wood had been so appointed. We offer him our congratulations and best wishes in his work.

As the Honorary Treasurer has told you, the financial position of the Society is satisfactory, in spite of the difficult times through which we are passing.

On your behalf, as well as on my own, I take this opportunity of thanking the Honorary Officers for their continued work on behalf of the Society. It is largely owing to the efforts of the Honorary Secretaries, Professor A. P. Elkin and Mr. D. P. Mellor, and the Honorary Treasurer, Mr. A. Clunies Ross, that the work of the Society proceeds so smoothly and so satisfactorily. We also express our appreciation of the work done by the Honorary Librarians, Mr. W. H. Maze and Dr. A. Bolliger, and Mr. H. W. Wood who was appointed Honorary Librarian on the resignation of Mr. Maze.

I regret to record the deaths of the following members during the year ending March 31st, 1944: John Job Crew Bradfield, Frederick Chapman, Archibald Howie and James Edward Mills.

JOHN JOB CREW BRADFIELD, D.Sc. (Eng.), was born at Sandgate, Queensland, in 1867, and was educated at Ipswich. He gained an Exhibition to the University of Sydney. In 1889 he graduated Bachelor of Engineering with first-class honours and the University Medal, and in 1896 he took the degree of M.E. On graduation in 1889 he was appointed draughtsman under Colonel Stanley, Chief Engineer for Railways, Brisbane. In 1891 he joined the Public Works Department, N.S.W., and was engaged on the design and construction of all classes of engineering works. He was sent abroad by the Government of N.S.W. in 1914 to visit the underground railways and long span bridges in Europe and America, and made a special study of traffic and train operation, and also made passenger traffic surveys of large underground stations throughout the world. In 1912 Dr. Bradfield was appointed Chief Engineer for Sydney Harbour Bridge and City Transit, and his scheme for Sydney's system of underground railways and the Harbour Bridge was adopted by Parliament. The City Railway construction cost more than seven million pounds sterling. In 1922 after preparing plans and specifications for the Sydney Harbour Bridge Dr. Bradfield was sent abroad again, to give information to prospective tenderers.

Dr. Bradfield was for a number of years a Member of the University Senate, also of the Town Planning Institution, of the Australian National Research Council, the Royal Society of N.S.W., the Commonwealth Engineering Standards Advisory Committee, and the Institution of Engineers, Australia. With Professor Warren and Mr. A. E. Cutler he established the Aviation School at Richmond, N.S.W., for the training of pilots during the war of 1914-1918. After the completion of the Sydney Harbour Bridge, on which he was engaged for seven years, Dr. Bradfield spent much of his time in Brisbane, having been appointed Consulting Engineer to the Queensland Bureau of Industry for the design, fabrication and construction of the Story Bridge, which spans the river at Brisbane, and has a total length of 1,463 feet as compared with the Sydney Harbour Bridge of 1,650 feet. He was also intimately concerned with the planning and design of the new University of Queensland. He investigated and strongly advocated a scheme to provide for an inland lake, and so make available enormous areas of otherwise desert country in the centre of Australia, his intention being to divert the flow of certain rivers from the sea to inland areas.

FREDERICK CHAPMAN, an Honorary Member of the Royal Society of N.S.W. since 1939, was born in London in 1864, and died on December 13th, 1943. He began his scientific career as an assistant to Professor Judd at the Royal College of Science, London. During the period of twenty years that he occupied this post he became an authority on the foraminifera, on which he published a text-book. He was appointed palæontologist to the National Museum, Melbourne, in 1902, and began his long study of the fossils of Australasia. He identified and arranged the palæontological collections of the Museum, and described and figured many rare specimens in papers published in scientific journals. He also published papers on palæobotany. He was appointed palæontologist to the Geological Survey of Victoria and was also part-time lecturer in palæontology at the University of Melbourne. He reported on the foraminifera of the Nimrod, Discovery and Funafuti expeditions. In 1927 he retired from the National Museum, and was engaged by the Commonwealth Government to report on specimens submitted in the search for oil. He retired from this work seven years later.

Chapman held office as president of the Royal Society of Victoria, of the Field Naturalists' Club of Victoria, and of the Microscopical Society of Victoria. He was member for Australia of the International Commission for Zoological Nomenclature. Among honours received by him were the Lyell Medal of the Geological Society of London, the Clarke Memorial Medal, the Australian Natural History Medallion, and the David Syme Prize. He was a tireless worker, and was always ready to help others and to give freely of his knowledge. In 1914 he published the first text-book on Australasian Fossils, and also wrote two popular volumes, "Open-Air Studies in Australia" and "The Book of Fossils". In all he published more than 500 papers on palæontological subjects and many on other subjects, in addition to many popular scientific articles.

ARCHIBALD HOWIE, a prominent Sydney business man, became a member of the Royal Society in 1936. He was Chairman of Directors of Howie, Moffatt and Co., and had held many important offices. He was an alderman of the City of Sydney, and was Lord Mayor in 1936 and 1937. He was president of the Royal Agricultural Society, also of the Sydney Chamber of Commerce, and for five years was president of the Jersey Herd Society, being himself a noted breeder of stock. He was elected to the Legislative Council in 1934, and served until his death. He was appointed Chairman of the Advisory Panel for Defence Works in July, 1939. He became a member of the Senate of the University of Sydney in the same year. Sir Archibald Howie was knighted in 1938.

JAMES EDWARD MILLS, who died very suddenly on May 11th, 1943, was born at Roma, Queensland, in 1905. He received his university education at the University of Queensland, and on completing his course there was awarded an 1851 Exhibition, and went to University College, London, where he took his Ph.D. degree. He returned to Australia, and was appointed to the Chemistry Department in the University of Sydney, retaining this post until his death.

Dr. Mills was particularly interested in spectroscopic research and in gas analysis, and analysed a number of specimens of oil and gas from Queensland bores, which had been put down to find one or other of these products. His spectroscopic work covered both emission and absorption spectra, and he taught the technique of absorption spectra measurement to graduates of Sydney and other Australian universities. During the years which have followed the outbreak of war Dr. Mills worked at the high pressure necessitated by shortage of staff and extra work imposed by the exigencies of war: it has been said of him by one of his colleagues that the idea in his mind was "to do the job, regardless of the consequences", and probably this continuous high pressure activity was in part responsible for his death while still in his prime.

Dr. Mills was Honorary Treasurer of the Australian Chemical Institute, and was a member of the Chemistry Man-power Committee for New South Wales. He also belonged to the Volunteer Defence Corps, and was a past president of the Sydney University Chemical Society and of the Sydney University Science Association.

PART II. THE SUCCESSION OF CARBONIFEROUS AND PERMIAN FLORAS IN AUSTRALIA.

In choosing as the subject of my address "The Succession of Carboniferous and Permian Floras in Australia", I have been prompted by a desire to add some small contribution to a subject which during the past fifteen or twenty years has received much attention from Australian geologists. I have been interested in the Carboniferous-Permian problem for more than thirty years, my first geological fieldwork having been carried out, in collaboration with Dr. W. R. Browne, on rocks of this age in the Pokolbin district. The results of that work were published in this Society's Journal in 1911. In spite of all that has been done, our knowledge of what Mr. F. C. Andrews referred to as the Permian problem in his recent Clarke Memorial Lecture is still far from complete. Until we are able to make a satisfactory correlation of the occurrences of Carboniferous and Permian strata in various parts of the Australian continent, it does not seem possible to determine just how the Australian succession fits in with the accepted succession in other parts of the world. Much remains to be done in the study of the faunas and floras preserved in these rocks, and once these are moderately well known, it remains to explain what may appear to be contradictory conclusions as to age arising from the study of different groups of animals and plants. On the whole, more satisfactory work seems to have been done with the faunas than with the floras. This is perhaps due to the fact that collecting of the faunas has made available more material for study and, perhaps as a consequence, there have been more palæontological workers on the faunas. Collection of the floras has been less concentrated—there has been comparatively little systematic collecting from specific horizons and consequently it is difficult, if not impossible, yet to recognize distinct horizons by the study of the contained fossil plants.

I have therefore chosen to speak in a more general way of the three distinct fossil floras in our Carboniferous-Permian succession, to indicate some of the relations of the elements in these floras with those of other continents, especially the southern continents, and to suggest some of the difficulties still to be surmounted in the exact correlation of the occurrences within Australia.

The three floras mentioned have been referred to respectively as (1) *Lepidodendron Veltheimianum* flora, (2) *Rhacopteris* flora, and (3) *Glossopteris* flora. The *Lepidodendron Veltheimianum* flora and the *Rhacopteris* flora are held to be of Carboniferous age; the *Glossopteris* flora is generally regarded to be of Permian age though a number of palæobotanists have suggested that it had its beginnings in the later part of the Carboniferous. This group of palæobotanists included the late Sir Albert Seward, Professor B. Sahni and Dr. A. L. du Toit, but I do not think I am alone in believing that a convincing case has not been made out for placing the appearance of the *Glossopteris* flora before the beginning of the Permian.

Professor Sahni, indeed (1926, Chart III) went so far as to place the Lower Marine Series, Lower Coal Measures, and Upper Marine Series of New South Wales all in the Carboniferous, though he placed both Lower Bowen and Upper Bowen Series of Queensland in the Permian.

(1) THE LEPIDODENDRON VELTHEIMIUM FLORA.

The *Lepidodendron Veltheimianum* flora, the oldest of the three floras, includes the following plants:

<i>Asterocalamites scrobiculatus</i> (Schloth.)	<i>Ulodendron minus</i> Lindley & Hutton
<i>Lepidodendron Veltheimianum</i>	<i>Stigmaria ficoides</i> Brongniart
Sternberg	<i>Clepsydropsis australis</i> Sahni
<i>Volkmannianum</i>	<i>Ancimites austrina</i> Etheridge
Sternberg	? <i>Rhacopteris</i> sp.
<i>Osbornei</i> Walkom	<i>Pitya Susmilchi</i> Walkom
sp. (Cf. <i>L. brevifolium</i>)	
sp. (Cf. <i>L. dichotomum</i>)	

These plants occur in the Upper Burindi and Lower Kuttung Series and their equivalents. They present a complete change from the flora of the Upper Devonian in which the most abundant plant was *Lepidodendron australe*, a species which does not persist into the Carboniferous and which is very distinct from the types of *Lepidodendron* known from the Carboniferous. *Lepidodendron Osbornei* is a type similar to *L. spetsbergense* which is known only from Lower Carboniferous of the northern hemisphere. *Pitya* too is known only from Lower Carboniferous rocks.

Recent examination by S. W. Carey and W. R. Browne (1938) of the relation between the marine Burindi Series and the freshwater Kuttung Series has resulted in the suggestion by these authors that the Lower Kuttung Series is of the same age as the Upper Burindi Series, and they place the age of these two series as Viséan, the upper of the two divisions of the Dinantian, the lowest division of the Carboniferous.

It is perhaps desirable at this point to make some reference to the confusion that may arise from the use of the terms Lower, Middle and Upper Carboniferous, in view of different meanings attached to these terms. The late R. Kidston, in his memoir on the Carboniferous flora of Great Britain, used only the terms Lower and Upper Carboniferous, making the line of division between the two at a floral break in the Millstone Grit.

This is the usual practice in Great Britain, as indicated by Seward (1941, p. 161), from whose table on page 261 it is seen that the European terms Westphalian and Stephanian correspond with the lower and upper portions of the Upper Carboniferous of Britain.

At a congress on Carboniferous Stratigraphy held at Heerlen in 1927 (Congrès pour l'avancement des Etudes de stratigraphie Carbonifère) a fourfold division of the Carboniferous was agreed upon, the system being divided into Dinantien, Namurien, Westphalien and Stephanien. (Heerlen, 1927, p. xliv.)

<i>Sphenophyllum speciosum</i> (Royle)	<i>Sphenopteris lobifolia</i> Morris
<i>emarginatum</i> Brong.	<i>alata</i> Lindley & Hutton
<i>Glossopteris Browniana</i> Brongniart	<i>Gondwanidium validum</i> (Feistmantel)
<i>indica</i> Schimper	<i>Cladophlebis Roylei</i> Arber
<i>ampla</i> Dana	<i>Noeggerathiopsis Hislopi</i> (Bunbury)
<i>angustifolia</i> Brongniart	<i>Dadoxylon Arberi</i> Seward
<i>angustifolia</i> var. <i>tænio-</i>	<i>farleyense</i> Walkom
<i>pteroides</i>	? <i>Psygmophyllum</i> cf. <i>flabellatum</i>
Seward	Lindley & Hutton
? <i>orbicularis</i> Feistmantel	<i>Walkomia australis</i> (<i>Brachyphyllum</i>
<i>tortuosa</i> Zeiller	<i>australe</i>) (Feistmantel)
<i>Jonesi</i> Walkom	<i>Samaropsis Dawsoni</i> (Shirley)
<i>decipiens</i> Feistmantel	<i>Etheridgei</i> Walkom
<i>spathulo-cordata</i> Feist-	<i>Pincombei</i> Walkom
mantel	<i>moravica</i> (Helmhacher)
<i>conspicua</i> Feistmantel	<i>Nummulospermum bowenense</i> Walkom
? <i>Mitchelli</i> Walkom	<i>Carpolithes circularis</i> Walkom
sp. (scale leaves)	<i>Carpolithus belmontensis</i> Walkom
<i>Vertebraria indica</i> Royle	<i>Cornucarpus striatus</i> Walkom
<i>Gangamopteris cyclopteroides</i> Feist-	<i>Cordaicarpus emarginata</i> Walkom
mantel	? <i>Pityolepis</i> sp.
<i>angustifolia</i> McCoy	<i>Dictyopteridium sporiferum</i> Feist-
<i>Sphenopteris polymorpha</i> Feistmantel	mantel

Various members of this flora occur in what we know in New South Wales as the Lower (Greta) Coal Measures and the Upper (Newcastle) Coal Measures. For the purposes of this address, in which I am dealing rather with the floras as a whole, I have not attempted to divide the flora according to the species present in the Lower and the Upper Coal Measures. Indeed, I am not quite certain that it would be possible to do so with any great degree of accuracy. The division of the Series containing this flora into Lower and Upper divisions in the occurrences scattered widely over Australia and their correlation with one another is still far from completely determined. In addition, too little attention has been given to detailed collecting to enable one to make accurate lists of the species which have been found at individual horizons.

However, the flora as a whole is completely different from the *Rhacopteris* flora. The only genera so far known to be common to the two floras are *Sphenopteris* and some of the genera of seeds such as *Samaropsis*, *Carpolithes*, *Cordaicarpus*. *Sphenopteris* is of course a form genus and the species recorded from the two floras are different. The seeds, as at present incompletely known, also represent different species in the two floras, and most of them are known only from impressions, few yet having been described with any indication of their structure.

We have, therefore, a flora which has nothing in common with the *Rhacopteris* flora, and one which is characterized by the appearance in notable abundance of a series of plants of quite new type—especially *Glossopteris* and *Gangamopteris*. It is thus reasonable to conclude that there is a considerable time break between the rocks containing the *Rhacopteris* flora and those containing the *Glossopteris* flora. What we have to consider most closely is whether this break may have been long enough to represent the time between Lower Carboniferous and Permian. Our main difficulty arises from the fact that our floras from the lower part of the Carboniferous may be compared directly with the Lower Carboniferous floras of the northern hemisphere, and Europe in particular, whereas the *Glossopteris* flora only bears comparison with similar floras in the various parts of Gondwanaland. The *Glossopteris* flora did indeed reach Russia some time

late in the Permian, but this does not help us in determination of the time of appearance of the flora in the southern hemisphere.

One thing that is remarkable in connection with the *Glossopteris* flora is the lack of precise knowledge of the nature of the plants which bore the leaves, *Gangamopteris* and *Glossopteris*. These two genera are extremely abundant in Permian rocks throughout the land areas which formed parts of Gondwanaland. There are a few known specimens which show leaves of *Glossopteris* attached to stems. It is presumed that *Vertebraria* was the rhizome of the *Glossopteris* plant but this has not been proved. From close association in a number of localities it is also believed that seeds referred to *Nummulospermum* were probably borne by the plant of which *Glossopteris* represents the foliage. But here again no definite proof has been produced of the actual connection of the seeds with the plant.

It has been generally agreed that *Gangamopteris* and *Glossopteris* are very closely related, and in restorations of the plants of Permian age, Seward (1941, p. 247) has shown both as represented by shrubs of similar habit to one another. There is some justification for this in the character of the specimens showing leaves attached to stems.

Recently, however, Dr. Teichert (1942) on the basis of a single *Gangamopteris* leaf, which appears to be imperfectly preserved in a marine series, has pictured *Gangamopteris* as a plant of very different habit. If his idea is correct and his determination of the leaf as *Gangamopteris* is also correct, it means some radical change in the view that *Gangamopteris* and *Glossopteris* are closely related plants. It were better, however, to await some further support for his contention, in view of the somewhat insecure foundation on which it is based.

Palaeontologists who have worked on the fossil content of the rocks in which the *Glossopteris* flora occurs, as well as of the associated marine series, mostly place them all in the Permian. Raggatt and Fletcher, after a detailed examination of the fauna in Western Australia and comparison with similar faunas in other parts of Gondwanaland, conclude (1937, p. 182): "The similarity in the faunas of the Kashmir, Indian and Australian sequences is so striking that contemporaneity and free communication between these regions may be assumed. We appear to be justified in concluding that beds characterized by the *Eurydesma-Conularia* fauna and the *Gangamopteris-Glossopteris* flora should be assigned to the Permian."

Among the genera of the *Glossopteris* flora there are a number which had already appeared in the European Carboniferous, e.g. *Annularia*, *Sphenophyllum*, *Sphenopteris*, *Psygomphyllum*, but generally there are specific differences between species of these genera from the two provinces. The southern hemisphere stems described as *Dadoxylon* and the leaves known as *Noeggerathiopsis* are also doubtless closely related to the northern genus *Cordaites*.

Some of the southern examples of *Annularia* probably show their closest affinity with species from the Shansi flora of Asia described by T. G. Halle who is of opinion that the beds containing them are of Permian age. *Annularia* cf. *stellata* described from near Dunedoo may be identical with *Lobatannularia inequifolia* Kawasaki or with *L. sinensis* Halle. Other similarities to this flora have been noted by Whitehouse who has recorded, but without description, the genera *Emplectopteris* and *Lobatannularia* from Queensland rocks.

Recent work in India (Palaeobotany in India, 1943) has shown the existence of a rich microflora in some of the Gondwanaland rocks containing the *Glossopteris* flora. D. D. Pant has examined some of the Bacchus Marsh tillite and B. Sahni some of the clay shale from the base of the Dwyka tillite from Vereeniging near Johannesburg. This work is being extended and samples from measured horizons of the Dwyka tillite are being examined by Pant. The results will be watched with interest and may yield important data for correlation purposes.

COMPARISON WITH THE SUCCESSION IN OTHER PARTS OF GONDWANALAND.

We may now turn to a comparison of the Australian succession with that in other regions. As noted before it is only the Lower Carboniferous floras that bear direct comparison with those in the northern hemisphere. It seems that Carboniferous (Lower Carboniferous especially) floras were cosmopolitan, groups made up of the same or very closely allied species occurring in continental areas of both northern and southern hemispheres. It may be that in the older rocks in which fossil floras are known we yet know insufficient of the plants preserved to enable us to determine the presence of floral provinces. In the Permian, however, there is sufficient evidence that there were distinct botanical provinces of which Seward (1941, p. 251) states that there were at least three. He refers to (1) what he calls the Atlantic-Chinese flora, including the Shansi flora which has affinities with floras of North America and Europe, (2) the Kusnezsk flora in Siberia extending from the Dwina River to Vladivostok, (3) the *Glossopteris* flora which is present in all those southern areas constituting what we generally know as Gondwanaland. These Permian floral provinces were the subject of discussion by Schuchert (1932) as well as by Seward (1941, pp. 234-287).

For useful comparisons for the Australian succession, it is therefore apparent that we can look chiefly to the floras of various parts of Gondwanaland.

South America.

The most complete comparison is obtained when we study the succession in western Argentina where, in the pre-cordilleran region, south of the town of San Juan, there is a wealth of fossil plant material. These plants occur in an area where there has been a considerable amount of tectonic disturbance, including much overthrusting. Dr. Harrington, when sending me some fossil plants for examination, said of this region, "The stratigraphical relations of the different fossil bearing horizons are unknown as the beds form part of a highly complicated thrust-structure of Alpine type and magnitude but of Hercynian age". As a result floras of apparent different ages occur in close geographical association and there has been a good deal of discussion as to their relative stratigraphical positions. Plants of Carboniferous and Permian ages occur at localities not far removed from one another, and these field occurrences have been used in support of the suggestion that the *Glossopteris* flora came into existence before the close of the Carboniferous.

Dr. Du Toit (1927) has given an account of a number of these occurrences (pp. 36-37) involving the presence of Carboniferous types closely associated geographically with typical Permian species. The Carboniferous forms include :

<i>Asterocalamites</i> <i>serobiculatus</i> (Schlotheim)	<i>Botrychiopsis</i> <i>Weissiana</i> Kurtz
<i>Lepidodendron</i> <i>aculeatum</i> Sternberg	<i>Rhacopteris</i> <i>Szajnochai</i> Kurtz
cf. <i>australe</i> McCoy	<i>inequilatera</i> var. <i>ovata</i> McCoy
<i>selaginoides</i> Sternberg	<i>Archaeopteris</i> <i>argentinae</i> Kurtz
<i>Veltheimianum</i> Sternberg	<i>Cardiopteris</i> <i>polymorpha</i> Goeppert
<i>Pedroanum</i> (Car-	<i>elegans</i> Kurtz
ruthers)	<i>Adiantites</i> <i>antiquus</i> (Ett.)
cf. <i>nothum</i> Unger	<i>Cordaites</i> sp.

The Permian species, indicating the presence of the typical *Glossopteris* flora, include :

<i>Phyllothea</i> <i>australis</i> Brongniart	<i>Glossopteris</i> <i>Browniana</i> Brongniart
<i>deliquescent</i> (Goeppert)	<i>indica</i> Schimper

Glossopteris retifera Feistmantel
Gangamopteris cyclopteroides Feistmantel
Gondwanidium validum (Feistmantel)
Cordaites (*Noeggerathiopsis*) *Hislopi*
 (Bunbury)

Noeggerathiopsis Whittiana (Feistmantel)
Rhipidopsis densinervis Feistmantel
ginkgoides Schmalhausen

Du Toit says of these, "Keidel has been to great pains in order to prove that there are actually *two distinct series* resting unconformably upon the older Palaeozoics, one with a flora including Lower and Upper Carboniferous forms and hence of Carboniferous age, overlain by the second formed of the glacials and the sediments with the *Glossopteris* flora, belonging to the Gondwana system and of 'Permian' age". He refers to the doubts as to the determination of precise horizons from which the different collections were obtained but admits that his limited opportunity for collecting did not enable him to dispel such doubts. He goes on, "In analysing these various collections, we observe further that in one locality or another some typical member of the 'northern flora' is in apparent association with some member of the 'southern' and this in so many ways that we have difficulty in escaping from the conclusion that all these various plants must probably have occurred intermingled on horizons intimately associated with the glacial series. It will, however, not be denied that the southern forms might perhaps have come from slightly higher levels within that particular series than those that yielded the northern elements, and it will therefore be conceded that *Gangamopteris*, *Glossopteris*, etc., if not actually accompanying *Rhacopteris*, *Cardiopteris*, etc., must occur shortly above this lowest plant-bearing carbonaceous zone *d*, with its northern Carboniferous flora.

"Granted that the data have been correctly interpreted (italics mine), the presence of *Gangamopteris*, *Glossopteris*, *Neuropteridium*, etc., would suggest that the whole of this conformable succession, down to its very base, resting discordantly upon pre-Carboniferous strata, should be regarded as forming part and parcel of the Gondwana System."

In 1926 Sahni had listed the Argentine plants in two groups, one as Lower Carboniferous, containing

Asterocalamites scrobiculatus
Lepidodendron sp. aff. *L. nothum*
Pedroanum
Botrychiopsis (? *Rhacopteris*) *Weis-*
siana

Rhacopteris sp. cf. *Machaneki*
Cordaites sp. cf. *borassifolius*
 ? *Rhabdocarpus*

The second group indicated as Carboniferous and Permian (mixed horizons), contained a mixture of what I have called in Australian floras the *Rhacopteris* flora and the *Glossopteris* flora.

I have searched carefully through Du Toit's description and can not find that he put forward any definite proof of the mixing of the two floras.

It is of interest to note that the succession of floras in this pre-cordillera region of western Argentina has a parallel in the succession of the faunas. Dr. H. Harrington has been working on the faunas in recent years and these, he says in a letter written in 1941, "range from Lower Carboniferous to Middle Permian".

I have dealt at some length with these Argentine floras since they are almost identical with our Australian floras of the same succession, and moreover because the strata containing the *Glossopteris* flora are closely associated with marine strata containing a fauna that shows close resemblances to the fauna of

our Permian marine series. In eastern Argentina Dr. Harrington refers to the marine fossils found in association with the *Glossopteris* flora and remarks that the faunule is "truly Australian in character".

One other feature in which the South American succession resembles the Australian is the complete absence of the northern Upper Carboniferous flora as represented by the *Neuropteris*, *Alethopteris*, *Pecopteris* group of plants. Du Toit does not make any comment on the absence of this group in Argentina.

South Africa.

In South Africa the succession is not represented as completely as in Australia, the Carboniferous elements being absent except for the occurrence of species of *Sigillaria* and *Lepidodendron* associated with the *Glossopteris* flora in the Eccia Series. In the Dwyka Series there is a record of a *Lepidodendron* which has been compared with *L. australe*, a species which in Australia is confined to the Devonian. There is some doubt in my mind as to the identity of the South African specimen with the Australian species—based on an examination I was able to make of the described specimen in South Africa. One interesting feature in South Africa is the occurrence of northern hemisphere Upper Carboniferous species in association with the *Glossopteris* flora in the coal measures at Wankie in southern Rhodesia. This interesting association has been described by Walton (1929), who has identified the following species from the Upper Wankie Sandstones:

<i>Phyllothea</i> sp.	<i>Asterothea</i> sp. A and B
<i>Sphenophyllum speciosum</i> (Royle)	<i>Cladophlebis</i> sp.
cf. <i>Thonii</i> Mahr	<i>Glossopteris indica</i> Schimper
<i>Thonii</i> var. <i>minor</i>	<i>Browniana</i> Brong.
Sterz.	<i>retifera</i> Feist.
<i>oblongifolium</i> (Germ.)	<i>tortuosa</i> Zeiller
cf. <i>Cyclodendron Lesliei</i> (Sew.)	cf. <i>angustifolia</i> Brong.
<i>Chansitheca</i> cf. <i>Kidstoni</i> Halle	<i>Cordaites Hislopi</i> Feist.
<i>Pecopteris unita</i> Brong.	
forma <i>emarginata</i>	
(Goepp.)	
<i>arborescens</i> (Schloth.)	
cf. <i>cyathea</i> Schloth.	

Walton refers to the presence "of a very pronounced northern element in the flora, including plants which are characteristic of the Upper Carboniferous and Lower Permian in western Europe, and some which occur in the Shansi Coal-field in China, and in rocks which are probably of Lower Permian age in Sumatra". Dr. Walton regarded this flora as indicating the age of the Upper Wankie Sandstones as Lower Permian or older.

India.

As regards the succession of floras, India offers little for comparison since the only typical Carboniferous assemblage consists of three species, viz. cf. *Rhacopteris inequilatera* (Feist.) (= *R. ovata*), cf. *Sphenopteridium furcillatum* (Ludwig) and cf. *Sphenopteris rigida* Ludwig, which occur in the Po Series (early Carboniferous) of Spiti. The Permian flora is of course very abundantly represented in rocks ranging from the Talchir Series to the Raniganj Series, and higher still the *Glossopteris* flora is found associated with the *Thinnfeldia* flora in rocks regarded as Triasso-Rhaetic in age.

Of species common to the Indian and Australian floras it may be of interest to note that *Neuropteridium* (*Gondwanidium*) *validum* is known in India only from the Karharbari Series, and *Glossopteris tortuosa*, *G. conspicua*, *Phyllothea robusta*, *P. indica* and *Cladophlebis Roylei* only from the Raniganj Series. Some of these species may be helpful in determining the ages of scattered occurrences in Australia.

CORRELATION OF THE PERMIAN SUCCESSION.

There are still many difficulties to be overcome in correlating the Permian succession in various parts of Australia. A typical area such as the Hunter River Valley presents the simple problem of two marine series and two freshwater series in the order Lower Marine, Lower freshwater, Upper Marine, Upper freshwater. There is much in common between the faunas of the two marine series, as there is also between the floras of the two freshwater series. It is known that the *Glossopteris* flora was in existence as far back as about the middle of the Lower Marine epoch, and that it continued at least till the close of the Upper Coal Measure epoch. Throughout that period of time the *Glossopteris* flora must have existed somewhere on the land surfaces of the continent, for it is inconceivable that it should have died out and appeared again without any notable change in its composition. It could be believed that when the marine seas receded they retreated beyond the limits of the present continent, and therefore that there may be a definite break between the deposition of the strata which we know to contain the Lower Marine and Upper Marine faunas. Whilst this is a possibility, it does not seem a probability, and with increased knowledge of the faunas and their ranges we should be able in time to trace the complete story of marine deposition from the beginning of Lower Marine time onwards. To arrive at a similar knowledge of the continuity of the floras will be much more difficult, for it seems reasonable to suggest that at any time during the life of the *Glossopteris* flora, on the continental area there may have been larger or smaller basins of freshwater deposition where plants could have been preserved. We are prone to think that any deposit of freshwater origin which contains remains of the *Glossopteris* flora should be correlated with either the Lower Coal Measures or the Upper Coal Measures. But there does not seem to be any reason why such isolated occurrences could not have been deposited at the same time as one of the marine series was being laid down. Thus the way to a complete understanding of the Permian problem still seems long and arduous. Much careful field work is necessary—both in tracing the stratigraphical relations of the strata from one district to another, and also in the careful collection of floras and faunas from definite horizons as an aid in determining the possibility of recognizing distinct zones by the contained fossils. One excellent piece of work has been done on the Carboniferous, viz. that of Drs. S. W. Carey and W. R. Browne, who have, as a result of careful field observations, suggested that the freshwater Lower Kuttung Series in New South Wales were deposited at the same time as the marine Upper Burindi Series. There is room for much work of this type on the Permian succession. An excellent basis for such studies should be available when it becomes possible to use the results of the extensive and careful field observations being made in the search for indications of oil in Australia.

Thus I seem to have shown only that, although the Permian problem has been the subject of many studies over a great number of years, there is ample work still to occupy a team of geologists on this one problem for a long period. So in this, as in many another problem, the fascination lies in the fact that with each advance in our knowledge there is opened up an ever-widening field for further investigation.

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EXTENSION OF MAXWELL'S EQUATIONS.

By P. FOULKES, B.Sc.

Communicated by PROFESSOR E. M. WELLISH.

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In rational units, Maxwell's equations for empty space are

$$\left. \begin{array}{l} \text{curl } \mathbf{E} + \dot{\mathbf{H}} = 0 \\ \text{curl } \mathbf{H} - \dot{\mathbf{E}} = \mathbf{J} \\ \text{div } \mathbf{E} = \rho \\ \text{div } \mathbf{H} = 0 \end{array} \right\} \begin{array}{l} \alpha \\ \beta \\ \gamma \\ \delta \end{array} \dots\dots\dots 1. \quad \dot{\rho} + \text{div } \mathbf{J} = 0 \dots\dots\dots 1a$$

The current density field is assumed to be non-rotational.

$$\therefore \mathbf{J} = \text{grad } \dot{\alpha} \dots\dots\dots 2$$

and 1a becomes

$$\dot{\rho} + \nabla^2 \dot{\alpha} = 0. \quad \therefore \frac{\partial}{\partial t} (\rho + \nabla^2 \alpha) = 0 \dots\dots\dots 1b$$

According to the recent claims by Ehrenhaft (1943), there is evidence for the existence of magnetic currents. This requires a modification in Maxwell's equations. The new equations will be valid from a theoretical point of view whether the isolation of magnetic charges and currents proves to be true or not, since in the latter case they would simply lead back to the original Maxwellian relations whenever applied to a specific problem.

Calling the magnetic current density $-\mathbf{M}$ and the magnetic charge density $+\mu$, we have

$$\left. \begin{array}{l} \text{curl } \mathbf{E} + \dot{\mathbf{H}} = +\mathbf{M} \\ \text{curl } \mathbf{H} - \dot{\mathbf{E}} = \mathbf{J} \\ \text{div } \mathbf{E} = \rho \\ \text{div } \mathbf{H} = +\mu \end{array} \right\} \begin{array}{l} \alpha \\ \beta \\ \gamma \\ \delta \end{array} \dots\dots\dots 3. \quad \left. \begin{array}{l} \dot{\rho} + \text{div } \mathbf{J} = 0 \\ \dot{\mu} - \text{div } \mathbf{M} = 0 \end{array} \right\} \begin{array}{l} \alpha \\ \beta \end{array} \dots\dots 3a$$

The current density fields are assumed to be non-rotational.

$$\therefore \left. \begin{array}{l} \mathbf{J} = \text{grad } \dot{\alpha} \\ \mathbf{M} = -\text{grad } \dot{\beta} \end{array} \right\} \begin{array}{l} \alpha \\ \beta \end{array} \dots\dots\dots 4$$

and 3a becomes

$$\left. \begin{array}{l} \dot{\rho} + \nabla^2 \dot{\alpha} = 0 \\ \dot{\mu} + \nabla^2 \dot{\beta} = 0 \end{array} \right\} \begin{array}{l} \alpha \\ \beta \end{array} \therefore \left. \begin{array}{l} \frac{\partial}{\partial t} (\rho + \nabla^2 \alpha) = 0 \\ \frac{\partial}{\partial t} (\mu + \nabla^2 \beta) = 0 \end{array} \right\} \dots\dots\dots 3b$$

We see from 3a that $\text{div } (\dot{\mathbf{H}} - \mathbf{M}) = 0$.

$$\dot{\mathbf{H}} - \mathbf{M} = \text{curl } \dot{\mathbf{A}}. \quad \mathbf{H} = \text{curl } \mathbf{A} + \int \mathbf{M} dt \dots\dots\dots 5$$

$$\text{Then } \text{curl } (\mathbf{E} + \dot{\mathbf{A}}) = 0. \quad \mathbf{E} = -\dot{\mathbf{A}} - \text{grad } \varphi \dots\dots\dots 6$$

From 3 β , 4 α , 5 and 6,

$$\left. \begin{array}{l} \text{curl curl } \mathbf{A} + \ddot{\mathbf{A}} + \text{grad } \dot{\varphi} = \mathbf{J} \\ -\text{div } \dot{\mathbf{A}} - \nabla^2 \varphi = \rho \end{array} \right\} \begin{array}{l} \alpha \\ \beta \end{array} \dots\dots\dots 7$$

Imposing on A and ϕ the restriction that $\text{div } A + \dot{\phi} = 0$ 8
we have

$$\left. \begin{aligned} -(\nabla^2 A - \ddot{A}) &= J \\ -(\nabla^2 \phi - \ddot{\phi}) &= \rho \end{aligned} \right\} \begin{array}{l} \alpha \\ \beta \end{array} \dots\dots\dots 9$$

Proceeding similarly, we see from 3β that $\text{div } (\dot{E} + J) = 0$.

$$\dot{E} + J = \text{curl } \dot{C}, \quad E = \text{curl } C - \int J dt \dots\dots\dots 10$$

$$\text{Then } \text{curl } (H - \dot{C}) = 0, \quad H = \dot{C} - \text{grad } \psi \dots\dots\dots 11$$

From 3α , 4β , 10 and 11

$$\left. \begin{aligned} \text{curl curl } C + \ddot{C} - \text{grad } \dot{\psi} &= +M \\ \text{div } \dot{C} - \nabla^2 \psi &= +\mu \end{aligned} \right\} \dots\dots\dots 12$$

Imposing the restriction that $\text{div } C - \dot{\psi} = 0$ 13

$$\left. \begin{aligned} -(\nabla^2 C - \ddot{C}) &= M \\ -(\nabla^2 \psi - \dot{\psi}) &= \mu \end{aligned} \right\} \begin{array}{l} \alpha \\ \beta \end{array} \dots\dots\dots 14$$

The form of the vector and scalar potentials is not affected by the extension of the theory since they still obey the differential equations set up in connection with the restricted theory. Hence with the usual assumptions

$$\left. \begin{aligned} 4\pi A &= \int \frac{[J]}{r} dv \\ 4\pi \phi &= \int \frac{[\rho]}{r} dv \\ 4\pi C &= \int \frac{[M]}{r} dv \\ 4\pi \psi &= \int \frac{[\mu]}{r} dv \end{aligned} \right\} \begin{array}{l} \alpha \\ \beta \\ \gamma \\ \delta \end{array} \dots\dots\dots 15$$

where the brackets indicate "retarded" values.

We can now find a relationship between the two generalised vector potentials A and C . For 3α and 3β become

$$\left. \begin{aligned} \text{curl curl } C + \text{curl } \dot{A} &= 0 \\ \text{curl curl } A - \text{curl } \dot{C} &= 0 \end{aligned} \right\} \begin{array}{l} \alpha \\ \beta \end{array} \dots\dots\dots 16$$

From these we can get two symmetrical relations by eliminating in turn C and A .

Curling 16β and differentiating 16α with regard to time, it follows by addition that

$$\text{curl}(\text{curl curl } A + \ddot{A}) = 0 \dots\dots\dots 17\alpha$$

Similarly, by curling 16α and differentiating 16β with regard to time, we obtain by subtraction

$$\text{curl}(\text{curl curl } C + \ddot{C}) = 0 \dots\dots\dots 17\beta$$

Equations 17 are symmetrical and constitute the most general relations obeyed by the vector potentials.

From 16α it follows that

$$\dot{A} + \text{curl } C = \text{grad } \omega \dots\dots\dots 18$$

$$\text{div } \dot{A} = \nabla^2 \omega = -\phi, \text{ by 8.}$$

$$\nabla^2 \omega + \dot{\phi} = 0 \dots\dots\dots 19$$

If $\text{grad } \omega = 0$, $\text{div } \dot{\mathbf{A}} = 0$, and $\ddot{\phi} = 0$.

$\therefore -\nabla^2 \phi = \rho$, by 9 β ,

and the equation of conservation of electric charge 3b α becomes

$$\frac{\partial}{\partial t} (-\nabla^2 \phi + \nabla^2 \alpha) = 0 \dots\dots\dots 20$$

$\therefore \Delta^2(\alpha - \phi)$ is a function of position only in this case.

These results can also be obtained from 17 α .

An entirely similar development can be derived for the vector potential C.

From 16 β , $\dot{\mathbf{C}} - \text{curl } \mathbf{A} = -\text{grad } \pi \dots\dots\dots 21$

$\text{div } \dot{\mathbf{C}} = -\nabla^2 \pi = \dot{\psi}$, by 13.

$$\therefore \nabla^2 \pi + \dot{\psi} = 0 \dots\dots\dots 22$$

If $\text{grad } \pi = 0$, $\text{div } \dot{\mathbf{C}} = 0$ and $\dot{\psi} = 0$.

$\therefore -\nabla^2 \psi = \mu$ and the equation of conservation of magnetic charge 3b β becomes

$$-\frac{\partial}{\partial t} (-\nabla^2 \psi + \nabla^2 \beta) = 0 \dots\dots\dots 23$$

$\therefore \nabla^2(\beta - \psi)$ is a function of position only in this special case.

As before, we can deduce these relations from 17 β .

Returning to equations 17, we see that these are the generalised wave equations

$$\left. \begin{aligned} \text{curl curl } \mathbf{H} + \ddot{\mathbf{H}} - \dot{\mathbf{M}} &= 0 \\ \text{curl curl } \mathbf{E} + \ddot{\mathbf{E}} + \dot{\mathbf{J}} &= 0 \end{aligned} \right\} \begin{matrix} \alpha \\ \beta \end{matrix} \dots\dots\dots 24$$

$$\left. \begin{aligned} \text{Now curl curl } \mathbf{H} &= \text{grad div } \mathbf{H} - \nabla^2 \mathbf{H} \\ &= +\text{grad } \mu - \nabla^2 \mathbf{H} \\ \text{and } \mathbf{M} &= -\text{grad } \beta \end{aligned} \right\} \dots\dots\dots 25$$

$$\left. \begin{aligned} \text{Also curl curl } \mathbf{E} &= \text{grad div } \mathbf{E} - \nabla^2 \mathbf{E} \\ &= \text{grad } \rho - \nabla^2 \mathbf{E} \\ \text{and } \mathbf{J} &= \text{grad } \alpha \end{aligned} \right\} \dots\dots\dots 26$$

Hence 24 becomes

$$\left. \begin{aligned} \nabla^2 \mathbf{H} - \ddot{\mathbf{H}} &= \text{grad } (\mu + \dot{\beta}) \\ \nabla^2 \mathbf{E} - \ddot{\mathbf{E}} &= \text{grad } (\rho + \dot{\alpha}) \end{aligned} \right\} \begin{matrix} \alpha \\ \beta \end{matrix} \dots\dots\dots 27$$

Equations 3 can thus be solved by using 27 and 3b.

Since \mathbf{E} and \mathbf{H} are additive fields, respectively, we see from 3 that the solution can be broken up into two sets of partial fields, one due to the electric currents and charges, the other to their magnetic analogues. Thus 3 can be replaced by

$$\left. \begin{aligned} \text{curl } \mathbf{E}_1 + \dot{\mathbf{H}}_1 &= 0 \\ \text{curl } \mathbf{H}_1 - \dot{\mathbf{E}}_1 &= \mathbf{J} \\ \text{div } \mathbf{E}_1 &= \rho \\ \text{div } \mathbf{H}_1 &= 0 \\ \dot{\rho} + \text{div } \mathbf{J} &= 0 \end{aligned} \right\} \left. \begin{aligned} \text{curl } \mathbf{E}_2 + \dot{\mathbf{H}}_2 &= +\mathbf{M} \\ \text{curl } \mathbf{H}_2 - \dot{\mathbf{E}}_2 &= 0 \\ \text{div } \mathbf{E}_2 &= 0 \\ \text{div } \mathbf{H}_2 &= +\mu \\ \dot{\mu} - \text{div } \mathbf{M} &= 0 \end{aligned} \right\} \dots\dots\dots 28$$

$$\text{together with } \left. \begin{aligned} \mathbf{E} &= \mathbf{E}_1 + \mathbf{E}_2 \\ \mathbf{H} &= \mathbf{H}_1 + \mathbf{H}_2 \end{aligned} \right\} \dots\dots\dots 29$$

SOME LOWER CRETACEOUS FORAMINIFERA FROM BORES IN THE GREAT ARTESIAN BASIN, NORTHERN NEW SOUTH WALES.

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Communicated by IDA A. BROWN, D.Sc.

With Plate I.

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INTRODUCTION.

A systematic examination is being made of samples obtained from bores drilled by the Water Conservation and Irrigation Commission of New South Wales in the Artesian Basin in the northern part of the State. It is hoped that the results obtained will help in working out the stratigraphy of the area and ultimately will assist in the solution of problems associated with the occurrence of subsurface water in the Basin. Neither the surface nor subsurface sediments in this area have been examined for a microfauna, but megafossils, including pelecypoda and scaphopoda, have been recorded from the Milparinka-Tibooburra district. Kenny (1934) states that these fossils "furnish positive evidence of the Lower Cretaceous (Rolling Downs) age of the beds and of definite affinity with the Roma Series of Queensland".

Samples from eleven bores have been examined to date and of these, seven have been found to contain an interesting microfauna of Cretaceous age. These bores are on the following properties :

- W. R. Johnston's "Calooma", 4 miles south-east of Lila Springs and 30 miles north-north-west of Bourke.
- G. M. Taylor's, 3 miles south of Ford's Bridge, and about 40 miles north-west of Bourke.
- E. Langbrien's Bullaroon Station, 30 miles north-east of Bourke.
- D. Murray's Goolgumble Station, 30 miles north-east of Bourke.
- A. Holmes's, near Ellaville, about 50 miles north-west of Bourke.
- Berawinnie Pastoral Co., Toorale Station, 50 miles west of Bourke.
- Borong No. 2 Bore, 40 miles north-east of Mungindi.

The foraminifera herein described are in the Commonwealth Palaeontological Collection, Canberra. The drawings of the species have been prepared by Mr. F. Canavan, M.Sc., of the Mineral Resources Survey.

PREVIOUS REFERENCES TO AUSTRALIAN CRETACEOUS FORAMINIFERA.

Despite the fact that sediments of Cretaceous age are fairly extensively distributed throughout Australia, there has been little investigation of them for microfossils in recent years.

The earliest worker was the late Professor W. Howchin, who in 1884 published a paper on foraminifera from a bore at Hergott Springs (now Marree), 441 miles north of Adelaide, in the Artesian Basin in South Australia, but did not describe any of them until 1895. In 1894 he listed 56 Cretaceous foraminifera from bores he had examined in the Artesian Basin, including fragments of

"*Bigenerina nodosaria*" from a bore near Wilcannia. Howchin commented "the most remarkable feature in the Table is the unusual proportion of foraminifera with arenaceous tests, there being no less than twenty species belonging to this class out of a total of fifty-six". The same feature is present in the collection now under discussion. There seems little doubt that the foraminifera from northern New South Wales belong to the same horizon as the South Australian forms.

In 1907, Howchin listed Cretaceous foraminifera from Gingin, Western Australia. Many of these specimens were later described by the late Mr. F. Chapman (1917).

REMARKS ON THE PRESENT COLLECTION.

The microfossils recorded from the bores in northern New South Wales include foraminifera, radiolaria and ostracoda. They occur in grey, carbonaceous shales. The association, in W. R. Johnston's Bore, of Cretaceous foraminifera and of radiolaria belonging to the genera *Cenosphaera*, *Porodiscus* and *Dictyomitra*, is known also from bores put down in the North-west Basin, Western Australia. (Crespin, 1938.) Ostracoda are only occasionally present, the commonest form being a well-known Cretaceous species, *Cytheropteron concentricum*.

Foraminifera are common in certain bores, arenaceous forms, especially *Haplophragmoides* and *Trochammina*, being strongly developed. Unfortunately, the majority of the tests have suffered compression and distortion and perfect specimens are difficult to obtain. (Howchin (1884) commented on the "compression and consequent distortion" of the South Australian specimens.)

Eight new species are herein described and notes on previously described species are included. The new species are:

Haplophragmoides chapmani.

Trochammina raggatti.

Trochammina parvula.

Spiroplectammina cushmani.

Marginulina subcretacea.

Lenticulina warregoensis.

Lenticulina gunderbookaensis.

Planulina cretacea.

DESCRIPTION OF SPECIES.

Genus *Hyperamminoides* Cushman and Waters, 1928.

Hyperamminoides sp.

Observations. Fragments of *Hyperamminoides* sp. are present in two bores, but in no case is any specimen well enough preserved to permit specific determination. Howchin recorded *H. vagans* Brady, a recent species of universal distribution, from the Hergott Springs Bore, South Australia, but it is probable that the two are the same and represent a new species.

Occurrence. W. R. Johnston's Bore, at 800 feet and 825 feet; and in No. 2 Bore, Boronga, at 1,701 feet and 1,751 feet 6 inches.

Genus *Ammobaculites* Cushman, 1910.

Ammobaculites australe (Howchin) (Pl. I, Fig. 1).

Haplophragmium sp. Howchin, 1884, p. 86.

Haplophragmium australis Howchin Ms., 1894, p. 364; 1895, p. 198, Pl. x; figs. 12-13.

Plesiotype. Test small, compressed, early portion coiled, later uncoiled in a straight linear series, which alters slightly in shape from being flattened at

base of series to oval at terminal. Five chambers in coiled portion, excavated at umbilicus. Sutures fairly distinct. Sutures in uncoiled portion less distinct, making it difficult to determine number of chambers present. Wall coarsely arenaceous and rough, composed of large grains of clear quartz and a dark mineral. Aperture simple, central. Length of test, 1.15 mm.; diameter of coiled chambers, 0.7 mm.

Observations. There is little doubt that this specimen is referable to Howchin's species, which was described from No. 1 Bore, Hergott Springs, South Australia, at a depth between 100 and 200 feet. He records further specimens from No. 2 Bore at 50 feet. The present specimen is smaller than that of Howchin's, the type measuring 2.9 mm. in length. The sutural lines in the linear portion of the present specimen are less distinct, Howchin's specimen showing five chambers.

A. australe closely resembles *A. subcretacea* Cushman and Alexander (1930) from the Lower Cretaceous beds at Lake Worth, near Fort Worth, Texas.

Occurrence. Plesiotype (Comm. Pal. Coll. No. 249), W. R. Johnston's Bore at 925 feet. Also D. Murray's Bore at 231 feet; and G. M. Taylor's Bore at 425 feet.

Genus *Haplophragmoides* Cushman, 1910.

Haplophragmoides chapmani sp. nov. (Pl. I, Figs. 2a, b, 3.)

Holotype. Test closely coiled, planispiral, compressed, deeply umbilicated, periphery rounded. Chambers distinct, 9 in last whorl. Sutures distinct, straight. Wall arenaceous, smooth, dark coloured. Diameter, 0.72 mm.; thickness, 0.29 mm.

Paratype. Test similar in structure to holotype, but larger, white in colour, and slightly distorted. Diameter, 0.86 mm.

Observations. *Haplophragmoides chapmani* is a common species in the samples from D. Murray's Bore, but, unfortunately, the majority of tests have been compressed and distorted. The striking features of the species, whether well preserved or distorted, are the very well marked and straight sutures and the pronounced umbilicus in all specimens. There is some variation in the size of the tests, the largest ones having a diameter of 1.2 mm.

Several species of *Haplophragmoides* are described from the Cretaceous of America, but they bear little resemblance to *H. chapmani*. This form is apparently similar to that recorded by Howchin from Hergott Springs as "(?) *Endothyra Bowmani*" for at first sight these two forms are similar in appearance.

This species has been named in honour of my esteemed predecessor as Commonwealth Palæontologist, the late Mr. F. Chapman.

Occurrence. Holotype (Com. Pal. Coll. No. 250), D. Murray's Bore at 277 feet. Paratype (Comm. Pal. Coll. No. 251), same bore at 165 feet. Also in Murray's Bore at 103 feet, 128 feet and 327 feet; in Holmes's Bore at 750 feet; G. M. Taylor's Bore at 300 feet; and in No. 2 Bore, Boronga, at 1,503 feet and 1,651 feet.

Genus *Spiroplectammia* Cushman, 1927.

Spiroplectammia cushmani sp. nov. (Pl. I, Fig. 7.)

Holotype. Test small, elongate, tapering with greatest width at apertural end; early chambers planispiral, later becoming biserial, the biserial portion making up the larger part of the test. Coiled portion consisting of small indistinct chambers. Five pairs of moderately inflated chambers in biserial part, with oblique, slightly depressed sutures. Wall finely arenaceous, white in colour.

Aperture narrow slit in inner margin of last formed chamber. Length of test, 0.78 mm.

Observations. *Spiroplectammina cushmani* is common in Murray's Bore at 103 and 125 feet, but the majority of specimens are broken or distorted. Its characters are distinct from any of the described species of *Spiroplectammina*. It bears a slight resemblance to *S. navarroana* Cushman (1932), described from the Cretaceous of Texas, in its inflated chambers in the biserial portion and in the small indistinct chambers in the coiled portion, but *S. cushmani* tapers more rapidly from the apertural end to the apex.

The species is named after Dr. J. A. Cushman, of the Cushman Laboratory for Foraminiferal Research, Sharon, Massachusetts.

Occurrence. Holotype (Comm. Pal. Coll. No. 255), D. Murray's Bore at 103 feet. Other specimens are at 125, 190 and 327 feet.

Genus *Trochammina* Parker and Jones, 1859.

Trochammina raggatti sp. nov. (Pl. I, Figs. 4a-c, 5.)

Holotype. Test very compressed, periphery lobulate, moderately acute; 6 chambers in last coil, distinct on dorsal surface, last chamber large and inflated, especially on ventral surface. Sutures distinct, straight. Surface moderately smooth. Chambers in early portion very small, increasing rapidly in size in adult portion. Wall finely arenaceous. Aperture on inner margin of last chamber extending on ventral surface from periphery almost to umbilicus. Colour chiefly brown except last chamber, which is white. Greatest diameter, 1.0 mm.; thickness, 0.29 mm.

Paratype. Test very compressed due to crushing, periphery lobulate, moderately acute, 6 chambers in last whorl, the last two being large and gently inflated. Chambers on dorsal side in early portion indistinct, sutures straight. On ventral side last chamber expanded, making flap over umbilicus. Aperture on inner margin of last chamber. Wall finely arenaceous, smooth, brown in colour. Diameter, 0.91 mm.

Observations. *Trochammina raggatti* is fairly common in the bores, especially in Murray's Bore, where specimens vary in size and in colour from white to brown. The majority of the tests have been compressed during sedimentation.

The species is comparable with *T. taylorana* Cushman, from Texas, in its compression, but the sutures in the former are straight and the last chamber is more inflated on the ventral surface. It differs from *T. diagonalis* (Carsey), a common species in the Cretaceous of America, in having straight sutures. The chambers in the early portion of *T. diagonalis* are less distinct and increase in size more rapidly than *T. raggatti*.

The species is named after the Director of the Mineral Resources Survey, Dr. H. G. Raggatt.

Occurrence. Holotype (Comm. Pal. Coll. No. 252), Dr. Murray's Bore at 327 feet. Paratype (Comm. Pal. Coll. No. 253), same bore at 231 feet. Also at the following depths: 103, 165, 190, 265 and 277 feet; in Holmes's Bore at 750 feet; and G. M. Taylor's Bore at 275 feet.

Trochammina parvula sp. nov. (Pl. I, Figs. 6a-c.)

Holotype. Test small, inequilateral, periphery lobulate, rounded. Chambers inflated, 6 in final whorl, increasing rapidly in size. Last chamber large and rounded on both dorsal and ventral surfaces. Chambers in early portion, small and indistinct. Umbilicus on ventral surface. Aperture ventral on inner margin of last formed chamber. Diameter, 0.34 mm.

Observations. *T. parvula* is a very small species, and there is no Cretaceous form with which it can be compared. In shape it resembles the recent *T. inflata* Montagu, but the last chamber of *T. inflata* is much larger and more inflated.

Occurrence. Holotype (Comm. Pal. Coll. No. 254), W. R. Johnston's Bore at 725 feet. Also found at 900 and 950 feet in that bore and in Murray's Bore at 265 feet.

Genus *Lagena* Walker and Jacob, 1798.

Lagena apiculata (Reuss).

Colina apiculata Reuss, 1851, p. 22, pl. i, fig. 1.

Lagena apiculata (Reuss) Chapman, 1917, pl. iii, fig. 24.

Observations. This species was originally described from the Cretaceous but its range extends up to Recent. One specimen is present in W. R. Johnston's Bore at 900 feet.

Genus *Lenticulina* Lamarck, 1804.

Lenticulina gunderbookaensis sp. nov. (Pl. I, Figs. 9a, b.)

Holotype. Test smooth, translucent, compressed, closely coiled, evolute, almost circular, periphery slightly keeled, sutures distinct, curved, slightly depressed. Nine chambers, increasing gently in size to final chamber. Aperture radiate but not prominent, at apex of apertural face. Length of test, 0.67 mm. breadth, 0.8 mm.

Observations. The flatness and circular character of the test of *Lenticulina gunderbookaensis* makes it distinct from any described species. It has been named after the County of Gunderbooka in which the bore is situated.

Occurrence. Holotype (Comm. Pal. Coll. No. 257), W. R. Johnston's Bore at 725 feet. Another specimen is recorded from No. 2 Bore, Boronga, at 952 feet.

Lenticulina warregoensis sp. nov. (Pl. I, Figs. 8a, b.)

Holotype. Test medium size, slightly elongate, oval, translucent, smooth, periphery acute. Peripheral outline evenly curved but faintly angular in last chamber. Chambers 10, early one involute, rapidly becoming evolute and increasing in size. Sutures smooth, curved, especially in early portion, where they are close together. Aperture radiate and protruding. Length, 1.1 mm.; width, 0.75 mm.

Observations. *Lenticulina warregoensis* shows some resemblance to *L. gibba* in shape, but the chambers in the present species are more numerous and the last chamber is not so elongate. Howchin's form "*Cristellaria gibba*" from Hergott Springs Bore is possibly referable to this species.

Several specimens of *L. warregoensis* are recorded from W. R. Johnston's Bore but none are complete enough for figuring. All are smaller than the holotype. The species is named after the Warrego River, which runs close to the bore site.

Occurrence. Holotype (Comm. Pal. Coll. No. 256), A. Holmes's Bore at 700 feet. Other specimens, Holmes's Bore at 400 feet; Johnston's Bore at 350, 400 and 575 feet; and in No. 2 Bore, Boronga, at 1,751 feet 6 inches.

Genus *Marginulina* d'Orbigny.

Marginulina subcretacea sp. nov. (Pl. I, Fig. 10.)

Holotype. Test elongate, earliest portion slightly coiled, rapidly uncoiling. Seven chambers in adult stage. Early portion slightly compressed, later

chambers becoming inflated, the last chamber, which has lost outer wall, being almost circular in section. Sutures distinct and slightly oblique. Wall ornamented with fine longitudinal costæ, except in earlier portion, which is smooth. Aperture radiate, in outer margin of last chamber. Length of test, 2.9 mm.

Observations. *Marginulina subcretacea* is represented by a single specimen. No close comparison can be made with any described Cretaceous species. The nearest form is *M. navarroana* Cushman (1937), described from Alabama, but it differs from it in the twisted character of the costæ in the earliest portion of the American species. *M. subcretacea* also bears some resemblance to the Recent and Tertiary species *M. costata* but the costæ are finer in the Cretaceous form and the test rounder.

Occurrence. Holotype (Comm. Pal. Coll. No. 258), A. Holmes's Bore at 450 feet.

***Marginulina bullata* Reuss.**

Marginulina bullata Reuss, 1845-1846, Pt. 1, p. 29, pl. xiii, figs. 34-38. Cushman and Jarvis, 1928, p. 96, pl. xiv, figs. 7, 8.

Observations. Specimens of this widely distributed Cretaceous species are recorded from W. R. Johnston's Bore at the depth of 825 feet, and from G. M. Taylor's Bore at 275 feet.

***Marginulina ensis* Reuss.**

Marginulina ensis Reuss, 1845-46, p. 29, pl. xii, fig. 13; pl. 13, figs. 25, 27.

Hemicristellaria ensis (Reuss) Plummer, 1931, p. 146, pl. x, figs. 1-4.

Marginulina ensis (Reuss) Cushman, 1937, pl. xiv, figs. 23-25.

Observations. One fairly typical specimen of this well known Cretaceous form is present in W. R. Johnston's Bore, at the depth of 1,075 feet. It has also been recorded from the Upper Cretaceous beds of Western Australia.

Genus *Anomalina* d'Orbigny, 1826.

***Anomalina rubiginosa* Cushman.**

Anomalina rubiginosa Cushman, 1926, p. 607, pl. xxi, figs. 6a-c; 1940, p. 31, pl. vi, figs. 1-3.

Observations. *Anomalina rubiginosa* described from the Velasco shale of Mexico, is a common Cretaceous species and several good specimens are present in Johnston's Bore. In the New South Wales specimens, the periphery is broadly rounded and the walls of the test perforate, especially on the ventral surface.

Occurrence. Johnston's Bore at 400, 425, 520, 725 and 750 feet, and G. M. Taylor's Bore at 325 feet.

Genus *Planulina* d'Orbigny, 1826.

***Planulina cretacea* sp. nov. (Pl. I, Figs. 11a, b, 12a, b.)**

Holotype. Test planispiral, dorsal face gently rounded, ventral face concave with small umbilicus. Periphery rounded. Six chambers in final whorl, gradually increasing in size and finely punctate. Sutures depressed, curved. Ventral surface of last chamber large and slightly inflated with aperture near margin. Diameter, 0.40 mm.

Paratype. Test similar in character to holotype but the test is larger with the last chamber showing strong inflation on the ventral surface. Diameter, 0.49 mm.

Observations. *Planulina cretacea* differs from *P. correcta* (Carsey), described from the Navarro beds in Texas, in its more evenly circular outline and more inflated chambers on the ventral surface. Several tests are present in W. R. Johnston's Bore. *P. cretacea* is most probably the species referred to by Howchin as "*Pulvinulina elegans*" from Hergott Springs.

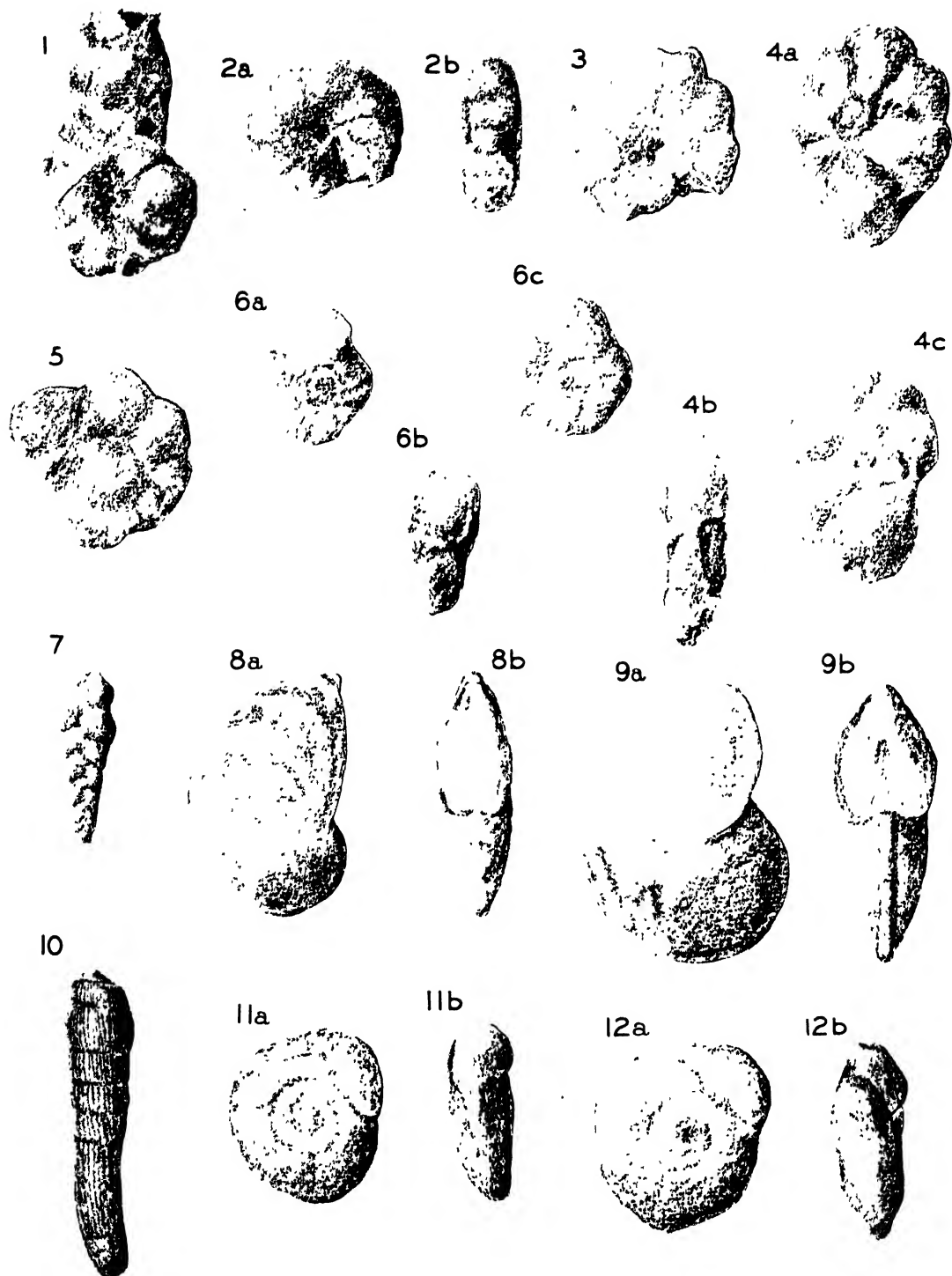
Occurrence. Holotype (Comm. Pal. Coll. No. 259), W. R. Johnston's Bore at 450 feet. Paratype (Comm. Pal. Coll. No. 260), W. R. Johnston's Bore at 400 feet. Also in this bore from 325 and 575 feet.

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EXPLANATION OF PLATE

- Fig. 1.—*Ammobaculites australe* (Howchin). W. R. Johnston's Bore, 925 feet. Plesiotype. $\times 30$.
- Fig. 2.—*Haplophragmoides chapmani* sp. nov. D. Murray's Bore, 277 feet. Holotype. (a) Side view, (b) apertural view. $\times 30$.
- Fig. 3.—*H. chapmani* sp. nov. D. Murray's Bore at 165 feet. Paratype. $\times 30$.
- Fig. 4.—*Trochammina raggatti* sp. nov. D. Murray's Bore, 327 feet. Holotype. (a) Dorsal; (b) apertural; (c) ventral. $\times 30$.
- Fig. 5.—*T. raggatti* sp. nov. D. Murray's Bore, 231 feet. Paratype. Dorsal view. $\times 30$.
- Fig. 6.—*Trochammina parvula* sp. nov. W. R. Johnston's Bore, 725 feet. Holotype. (a) Dorsal; (b) apertural; (c) ventral. $\times 60$.
- Fig. 7.—*Spiroplectammina cushmani* sp. nov. D. Murray's Bore, 103 feet. Holotype. $\times 30$.
- Fig. 8.—*Lenticulina warregoensis* sp. nov. A. Holmes's Bore, 700 feet. Holotype. (a) Side view; (b) apertural. $\times 30$.
- Fig. 9.—*Lenticulina gunderbookaensis* sp. nov. W. R. Johnston's Bore. 725 feet. (a) Side view; (b) apertural. $\times 60$.
- Fig. 10.—*Marginulina subcretacea* sp. nov. A. Holmes's Bore, 450 feet. Holotype. $\times 15$.
- Fig. 11.—*Planulina cretacea* sp. nov. W. R. Johnston's Bore, 450 feet. Holotype. (a) Dorsal; (b) apertural. $\times 60$.
- Fig. 12.—*P. cretacea* sp. nov. W. R. Johnston's Bore, 400 feet. Paratype. (a) Dorsal; (b) apertural. $\times 60$.



A NOTE ON THE RÔLE OF THE NITROSYL GROUP IN METAL COMPLEXES.

By D. P. MELLOR, M.Sc.,
and D. P. CRAIG, M.Sc.

Manuscript received, March 15, 1944. Read, April 5, 1944.

The purpose of this note is twofold : firstly to clear up certain inconsistencies in the literature relating to the magnetic behaviour of two nitrosyl cobalt compounds ; and secondly to discuss the different rôles played by the nitrosyl group in various metal complexes.

When nitric oxide is bubbled through an ammoniacal cobalt solution, the gas is slowly absorbed and a black or pink nitrosyl complex is formed according as cobaltous chloride or cobaltous nitrate forms the starting material (Sand and Genssler, 1903 ; Werner and Karrer, 1918). Pauling (1939) has discussed the structure of $[\text{Co}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$ (black) in terms of a magnetic moment of 2.81 Bohr magnetons* while Frazer and Long (1938) have described a hydrated form of the compound, $[\text{Co}(\text{NH}_3)_5\text{NO}]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ (colour not mentioned) with a magnetic moment of 4.12 Bohr magnetons. The method of preparation used by Frazer and Long is that which has repeatedly given the black form in this laboratory. Under the same conditions, Milward, Wardlaw and Way (1938) also obtained the black anhydrous complex for which they reported a magnetic moment of 1.63 Bohr magnetons. This value agrees reasonably well with the values we have obtained with a number of different specimens : 1.66, 1.55, 1.56 Bohr magnetons.

Milward *et al.* (1938) propose a structure for $[\text{Co}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$ in which the cobalt atom exhibits a variable valency owing to resonance. Since the valence states proposed involve different numbers of unpaired electrons, resonance between them is not possible (Pauling 1939) and the suggested structure is therefore not satisfactory. The following structure is consistent with the magnetic data :

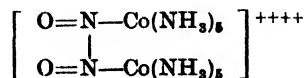


Fig. I.

This makes the complex ion dimeric, the two halves being linked through the nitrosyl nitrogen. There would thus be two unpaired spins for the dimer but calculation on the assumption that the substance is a monomer would give a moment corresponding to one unpaired spin. This explanation assumes that cobalt is bivalent and covalently bound to the six surrounding nitrogen atoms by d^2sp^3 bonds. It is difficult to be sure about the correctness of this latter assumption, especially when it is recalled that in $[\text{Co}(\text{NH}_3)_6]^{++}$ the Co-N bonds are ionic in character. Ionic bonds, however, would give rise to moments in the neighbourhood of 3.88 Bohr magnetons, well outside the range of the observed moments. It must be admitted that the proposed structure (Fig. I)

* This is the value obtained by Bose (1930).

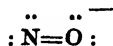
has other shortcomings; for one thing it does not explain why this particular complex ion is formed with the chloride and not the nitrate.

It is a significant fact that by treatment with hydrochloric acid, nitric oxide can be expelled from $[\text{Co}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$ but not from $[\text{Co}(\text{NH}_3)_5\text{NO}](\text{NO}_3)_2$, nor from $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ nor from $\text{K}_3[\text{Mn}(\text{CN})_5\text{NO}]$. The black compound $[\text{Co}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$ resembles $\text{K}_3[\text{NiNO}(\text{S}_2\text{O}_3)_2]$ in the sense that the latter also yields nitric oxide on treatment with hydrochloric acid. The rôle of nitric oxide in these last two compounds may therefore be quite different from that in the other two classes of nitrosyl complexes now to be dealt with. While the above formulation of the black compound may leave its constitution as uncertain as ever, the formulation of the structure of remaining nitrosyl complexes offers no great difficulty.

In agreement with Bose (1930) and Milward *et al.* (1938) we find that the pink compound $[\text{Co}(\text{NH}_3)_5\text{NO}](\text{NO}_3)_2$ is diamagnetic, from which it may be inferred that the cobalt is in the tervalent condition and is linked to the six surrounding atoms by d^2sp^3 bonds. This structure implies that the nitrosyl group produces the same effect on the charge of the complex ion as does chlorine in $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{++}$. Nitric oxide is an odd molecule with the structure



and the gas is therefore paramagnetic. In the formation of the pink complex, nitric oxide may be regarded as oxidising Co^{II} to Co^{III} , becoming in the process NO^- , which, having the structure



contributes nothing to the paramagnetism of the complex ion. When nitric oxide is substituted for NH_3 in $[\text{Co}(\text{NH}_3)_6]^{+++}$ to form $[\text{Co}(\text{NH}_3)_5\text{NO}]^{++}$ it functions precisely as it does in diamagnetic NaNO .

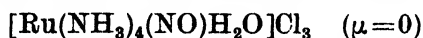
There is, however, another way in which the nitrosyl group can function in a complex ion, as a consideration of the constitution of the nitroprusside ion will serve to show. Before the rôle of the nitrosyl group can be determined, the valency of the central metal atom of the complex ion must first of all be decided. There is some conflict of opinion about the valency of iron in $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$, Weinland (1924) and Bray and Latimer (1940), for example, holding that the iron is tervalent, while Emeleus and Anderson (1938) regard it as bivalent. The question can be decided on the magnetic behaviour of the compound which favours the view that the iron is bivalent and forms d^2sp^3 bonds just as it does in diamagnetic $[\text{Fe}(\text{dipy})_3]\text{Cl}_2$. If we accept the view of Emeleus and Anderson that iron in nitroprussides is in the ferrous condition, then the nitrosyl group affects the charge of the complex ion as though it entered as NO^+ ($:\text{N} \equiv \text{O}:^+$). That is to say NO reduces iron in $[\text{Fe}(\text{CN})_6]^-$, becoming in the process NO^+ , which then displaces one of the CN groups to form $[\text{Fe}(\text{CN})_5\text{NO}]^-$. The nitrosyl group functions here in the same manner as in $(\text{NO})_2[\text{SnCl}_6]$.

If the nitrosyl group functioned as a negative group in $[\text{Fe}(\text{CN})_5\text{NO}]^-$, we should have to regard the valency of the iron as four, in which case nitroprussides should be paramagnetic with a moment of approximately 2.85 Bohr magnetons. This is the moment predicted for Fe^{IV} when it forms d^2sp^3 complexes (Pauling, 1939) but unfortunately no data have been reported for complexes of this type.

In order to explore the question further and to obtain additional evidence in support of the above views we have studied the manganese complex $\text{K}_3[\text{Mn}(\text{CN})_5\text{NO}]$ recently prepared and described by Blanchard and Magnusson (1941).

A manganese compound was chosen because Goldenberg's (1940) extensive magnetic studies of compounds of this metal in which the oxidation states range from +1 to +7, enable the nitrosyl complex to be used as a favourable test case. $K_3[Mn(CN)_5NO]$ is diamagnetic and in this respect resembles $K_3[Mn(CN)_6]$ from which it is concluded that Mn in $K_3[Mn(CN)_5NO]$ is monovalent. Had the nitrosyl group functioned as it does in $[Co(NH_3)_5NO](NO_3)_2$, a moment of 2.83 Bohr magnetons would be expected, for this is approximately the value of the moment found for $K_3[Mn(CN)_6]$ by Ray and Bhar (1928).

It is interesting to speculate whether it is a general rule for nitric oxide to function as a negative group in cationic complexes and a positive group in anionic complexes. That the former is true there can be little doubt, since there is no record of the substitution of positive groups in cationic complexes, and there is no reason for believing that nitric oxide should be exceptional in this respect. We should thus regard ruthenium as quadrivalent in



If the above rule regarding substitution in anionic complexes is general, we should regard Ru as bivalent in $K_2[RuCl_5NO]$. Unfortunately magnetic data do not permit an unequivocal distinction between Ru^{II} and Ru^{IV} . It is known that the ammines of Ru^{II} are diamagnetic, as they should be if they follow Pauling's rules, but Ru^{IV} complexes are not always paramagnetic with $\mu=2.83$ as required by theory. They are sometimes diamagnetic as is the case with $K_2[RuCl_5OH]$ (Mellor, 1943). Compounds of osmium such as $K_2[OsCl_5NO]$ offer no better prospects for testing, by magnetic methods, these views on the constitution of nitrosyl complexes of the platinum metals, but in the absence of any evidence to the contrary it is reasonable to suppose that what holds for the nitrosyl complexes metals of the iron transition series also applies to metals of the palladium and platinum series.

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We are indebted to Mr. J. S. Burkitt for the preparation of specimens of $K_3[Mn(CN)_5NO]$ and $K_3[Ni(S_2O_8)_2NO]$.

THE GEOMORPHOLOGY OF THE CENTRAL EASTERN AREA OF NEW SOUTH WALES.

PART I. METHODS OF LANDFORM ANALYSIS FROM TOPOGRAPHIC MAPS.

PART II. LANDFORM ANALYSIS OF THE ORANGE-BATHURST DISTRICT.

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(From the Department of Geography, University of Sydney.)

(With two maps and three text-figures.)

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CONTENTS.

	Page
Introduction	28
Part I—	
(1) Topographic Data Available	29
(2) Methods of Landform Analysis	30
(a) Altimetric Frequency Curves	30
(b) Strip "High-Point" Profiles	32
(c) Reconstructed or Generalised Contours	33
Part II—	
(1) Altimetric Frequency Curves for the Orange-Bathurst District	35
(2) Strip "High-Point" Profiles for the Orange-Bathurst District	37
(3) Reconstructed or Generalised Contours for the Orange-Bathurst District	39
Summary	40

INTRODUCTION.

In recent years many geographers and geologists have directed their research towards the detection of erosion surfaces in regions of polycyclic relief. In these studies some new techniques of landform analysis have been developed, and, as they do not appear to have been used in Australia it seems desirable to examine them briefly, suggest improvements or changes to meet local conditions, and apply them to those areas in New South Wales for which topographic maps are available.

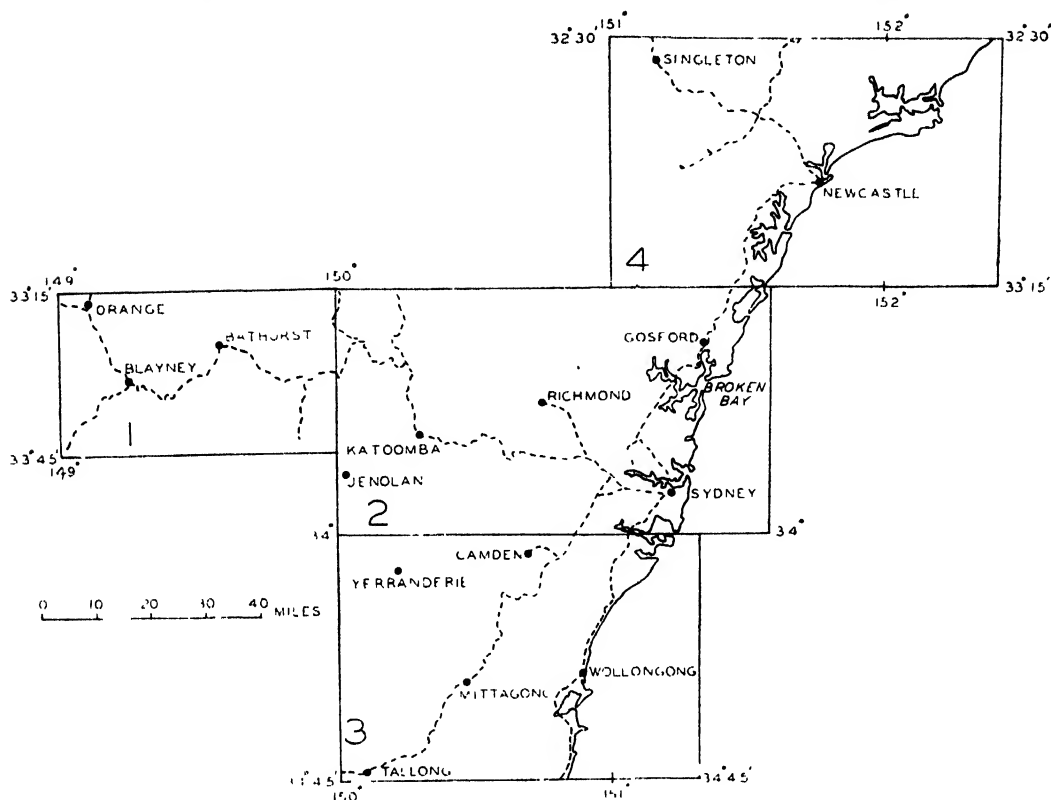
The techniques which enable one to recognise and describe erosional surfaces may also aid in the detection of structural surfaces. With this in view it is proposed, in this and subsequent papers, to examine from field studies and from the topographic maps, the landforms of the Central Eastern area of New South Wales.

The term Central Eastern Area is used to define the area as set out in Map 1.

For the sake of convenience the area has been arbitrarily divided into four districts, which have been called

- (1) The Orange-Bathurst District ;
- (2) The Katoomba-Broken Bay District ;
- (3) The Mittagong-Wollongong District ;
- (4) The Lower Hunter Valley District.

When each of these districts has been examined, data will be available to consider the area as a whole.



Map 1.

The Central Eastern Area of New South Wales.

- (1) The Orange-Bathurst District.
- (2) The Katoomba-Broken Bay District.
- (3) The Mittagong-Wollongong District.
- (4) The Lower Hunter Valley District.

PART I. METHODS OF LANDFORM ANALYSIS FROM TOPOGRAPHIC MAPS.

(1) Topographic Data Available.

The only topographic data which are of value and readily available in New South Wales for detailed landform studies are the maps of the Military Survey of Australia. These have been prepared by the Australian Section of Imperial General Staff and are printed at Melbourne. They are on the scale of one inch to one mile (1 : 63,360) and have a contour interval of 50 feet. Maps covering the coastal area from Port Stephens in the north to Jervis Bay in the south and extending varying distances inland have been available since 1939. The more recent editions of this map series are gridded, the grid lines divide the maps into areas 1,000 yards square and so readily present small units suitable for any statistical methods of relief analysis.

The accuracy of topographic analysis from maps is limited by the accuracy of the maps on which the analysis is based. The contours on the maps of the Military Survey of Australia are not surveyed, but are interpolated from vertical control points. The accuracy of the maps, as set out by T. A. Vance (1940), is as follows :

“ (i) *Horizontal Accuracy of Planimetric Detail.* 95% of all well defined cultural and drainage features shall be plotted on the map in correct horizontal coordinate position within 1/50 inch, at the publication scale.

"(ii) Vertical Accuracy of Topographic Detail.

"Contours. 85% of all elevations interpolated from the map contours shall be correct within half the contour interval. Not more than 5% of all elevations interpolated from the map shall show errors in excess of the contour interval. Also, any contour which can be brought within the above noted vertical tolerance by shifting its plotted location by 1/25th inch (1 mm.) in any direction, at the publication scale, shall be considered as correctly plotted.

" 'Spot' Elevations. All spot elevations shown on the map shall be correct to within one-quarter of the contour interval . . ."

The data provided are therefore altogether too coarse for the accurate determination of many minor features in the landscape where the relative relief is 50 feet or less. Thus in the study of longitudinal and cross profiles of river valleys where minor breaks of slope are important, the maps have to be supplemented by field-survey. Similarly they do not provide enough detail for the recognition of minor marine terraces. Apart from these more refined studies the maps provide ample data of a sufficiently high order of accuracy for the determination of major erosional and structural surfaces, which usually have a relative relief in excess of the contour-interval of the maps. If statistical methods only are used, and the study is carried out over large areas, the information provided is sufficient for a valid statistical examination and deduction.

When the contour data are used to generalize the maps, so as to reconstruct the now dissected surfaces, there are sufficient accurate data to serve all requirements. In fact, there is such a wealth of detail in the areas of high relative relief that some means have to be devised to generalize the maps so as to discover facts about the landforms which are not at all obvious by mere inspection of the map.

(2) Methods of Landform Analysis.

On sheets of tracing paper copies of the small uniform 1,000 yards grid-squares for the whole area were prepared. In each square the height of the highest point in the corresponding square of the topographic map was recorded. The value of the height of the highest point in each square was plotted as the height shown by the contour encircling the highest area in each square and reckoned as having a value ranging up to 50 feet above that height.

It is obvious that the size of the mesh of readings is of particular significance. With this in mind a coarser and a finer mesh of readings were tested. A coarser mesh of 4,000 yards square was found in some areas to give insufficient information. It masked or did not record sufficient data to reveal what appeared to be significant breaks of slope on the topographic map. A finer mesh of readings (250 yards square) was found in sample areas, to give essentially the same results as the 1,000 yards grid-squares. It was thus considered that the highest point in each of the 1,000 yards grid-squares was a sufficiently fine mesh of heights for the analysis and reconstruction of the major landform surfaces. The highest point or summit-heights alone are recorded as these are, in theory, the most significant altitudes on a dissected planation surface. Thus, for instance, over the 2,000 square miles in the Orange-Bathurst District the values of the "high points" in the 6,230 small squares were recorded. This information is all that is required in the following three methods of analysis.

(a) Altimetric Frequency Curves.

The method of landform analysis by the construction and use of Altimetric Frequency Curves has been applied with considerable success by H. Baulig (1928) in France and by S. E. Hollingworth (1938) in Britain. It consists of the

statistical analysis of "spot heights"¹ or the heights deduced from the contours of the highest points in uniform squares on topographic maps. The values of the heights are listed and arranged so as to give the frequency of occurrence of each height. From the frequencies a frequency curve is constructed showing the altitudinal distribution of such "high points" over the area. (See Figures 1 and 2.)

On the curve a well-marked frequency maximum indicates the presence of fairly level benches or platforms, while a sharp drop in the curve, to a frequency minimum, indicates a preponderance of steep slopes. Thus the occurrence of well-defined maxima at certain altitudes and the absence of such frequencies at intermediate altitudes indicate that the profile of the land flattens when these particular altitudes are approached and steepens above and below these altitudes.

In practice the frequency curve may show a number of peaks or maxima, and it is possible that some of them are accidental and have no valid interpretation. Those maxima which are more pronounced than the rest would appear to have more real significance. The significance of the maxima can be tested in several ways. In the first place independent curves could be constructed for parts of the area and a marked recurrence of maxima and minima values at the same altitudes on the different curves would offer strong support for the deductions. The curves are probably best tested against the original topographic maps of the area and by field survey. This testing and close watch on the deductions that may be drawn from the curves is necessary to distinguish between those features of the curve which are significant and those which may be due to the method itself and the nature of the terrain examined.

Baulig (1928), who appears to have been the first to apply and test the method, has used it mainly to locate high-level, horizontal or marine benches, and he points out (Baulig, 1935) that "horizontal benches at constant altitudes, if any such exist, will evidently determine a greater frequency of points about these altitudes while ancient surfaces of erosion being presumably more or less deformed in various manners, will have no such effect".

Miller (1939), in commenting on the method, states: "The method fails, however, to detect or include bevelled spurs and gently sloping surfaces which are yet not quite flat."

These statements by Baulig and Miller both assume that the frequency of occurrence of each individual "spot-height" only is plotted or that the altitudinal unit is small. That is certainly the method necessary to detect horizontal benches. The technique has still a wider application and can be used to indicate the occurrence and nature of gently-sloping surfaces and ancient surfaces of erosion.

If, instead of plotting the frequency of occurrence of each individual height, the heights are grouped into wider ranges of altitude, say the range of 50 feet or 200 feet, then gently sloping surfaces with these altitudinal ranges are indicated by frequency maxima.

This method has been applied in Part II to the Orange-Bathurst District, Figures 1 and 2, where as far as we know there is no evidence of or no necessity to postulate high levels of eustatic origin.

In Figure 1 the frequencies have been plotted with the heights arranged as having an interval of 50 feet. In some cases the figures need to be rearranged with a greater range of altitude than 50 feet. Two problems now arise, firstly, what altitudinal range should be adopted, and secondly, how will one rearrange the frequencies into the new range group? The latter problem is best illustrated

¹ "Spot-heights" is a common technical term applied to data in European maps and refers to heights above datum level printed close to a dot on the map. They are generally located on high points and must be distributed uniformly over the map to be of any value in this work.

as follows. The values in Figure 1 could be rearranged into an altitudinal range of 200 feet with the divisions occurring at either the odd or even hundreds. The following table gives values for this new arrangement.

Altitudinal Range.	Frequency.	Altitudinal Range.	Frequency.
3,600-3,400	430	3,700-3,500	423
3,400-3,200	863	3,500-3,300	656
3,200-3,000	1,397	3,300-3,100	1,242
3,000-2,800	851	3,100-2,900	1,173
2,800-2,600	619	2,900-2,700	729

It is obvious from the grouping of the frequencies that despite the incidence of the altitudinal unit a maximum frequency occurs at or about 3,100 feet. The incidence of the altitudinal unit may reduce or magnify a break in the curve but it does not eliminate it. The method has only a limited usefulness and requires to be used and tested against other methods and field evidence.

(b) Strip "High Point" Profiles.

Sections or profiles are widely used in illustrating landform studies. Composite or projected profiles have been used extensively by Barrell (1920), Miller (1937) and others. The composite profile is constructed by selecting and emphasising the higher parts only of a series of profiles along parallel lines. The latter results are analogous to a panorama skyline. In the projected profiles the less elevated features are included where not obscured by higher areas. Great care is required in selecting a suitable belt for projection and not all areas, especially extensive areas, can be suitably represented by this method. In both these methods the sections or profiles are drawn from the height values of the contours intersected by a line drawn across the topographic map. The sections thus include a large amount of detail of minor valley dissection which is then generalised or smoothed out in the final profiles. Where the object however is to illustrate major erosional surfaces, it is suggested here that it is best to dispense in the first instance with a large amount of the detail and to select and plot the significant "high-point" values.

If the "high-points" as selected and used for the construction of the altimetric frequency curves are again considered we have the necessary data to draw high-point profiles of the area. If a "high-point" profile is required, then the elevation in any set of squares running in a straight line across the map may be plotted, the elevations being considered as occurring at intervals of 1,000 yards. A strip or composite high-point profile may be constructed by taking, say, three adjacent sets of squares and plotting a composite high-point profile from this set of data. Thus the "strip high-point" profile can be constructed from the highest point occurring in a strip 3,000 yards wide and at intervals of 1,000 yards along the line of section. Separate profiles may be drawn for strips which are 10,000 yards apart from centre to centre. Such a group of profiles as in Figure 3 is a summary or reconstruction of the high-point elevations of 30% of the total area and this is considered to be the essential requirement for an analysis of the major landforms and erosion surfaces of most areas. By plotting only the high points, many minor features due to more recent dissection are eliminated and the major erosional surfaces or structural features of the landscape are portrayed and emphasised.

(c) *Reconstructed or Generalised Contours.*

It has been pointed out by Wooldridge and Morgan (1937) that "when it is required to study the major physiographic facets of an area, it is well to dispense with the complicating detail produced by minor valley dissection. For this purpose generalised contours may be drawn so as to bring out the form of the local summit planes."

No attempt, however, has apparently ever been made to reconstruct² from the information on topographic maps, a contour map for an extensive area dispensing with the detail of minor valley dissection and showing the former extent of dissected summit planes.

It is suggested here that when it is desirable to attempt to reconstruct the contours of the summit planes of an extensive area the following method could be followed. The "high-points" plotted in each of the 1,000 yard-squares, and used above for other methods of analysis may be regarded as a set of spot levels occurring in the centre of each square. Such a series offers a suitable mesh of heights from which contours, with 200-foot vertical interval, can be drawn by the usual methods of interpolation.

As the spot levels are, in this case, the high points over the surface, then contours drawn with them as a basis will reconstruct the high-point surface and will give a good approximation of the former extent of the various summit planes.

The method can only be applied with any certainty in those areas where broad stretches of the summit planes remain. If denudation of the surface has so progressed that the summit plane is consumed and the interfluves are sharp-crested ridges, then the summit elevations of the latter will have been lowered. The high-point values of such ridges and isolated hills must be ignored in some cases or recompensed for lowering in the drawing of the contours and their subsequent smoothing. If the topography is suitable the method can be rigidly and consistently applied to topographic maps and produces a result which is more useful than either of the preceding methods.

In Map 2 the high-point surface of the Orange-Bathurst District has been reconstructed by using the high points as spot levels and drawing the contours at 200 feet vertical intervals. The value of such a reconstruction is evident. The "high point" profiles illustrate the features in section; this map gives them in plan and shows the various summit-planes in extent and elevation.

The value of the results of the three methods depends upon a number of factors, but mainly upon

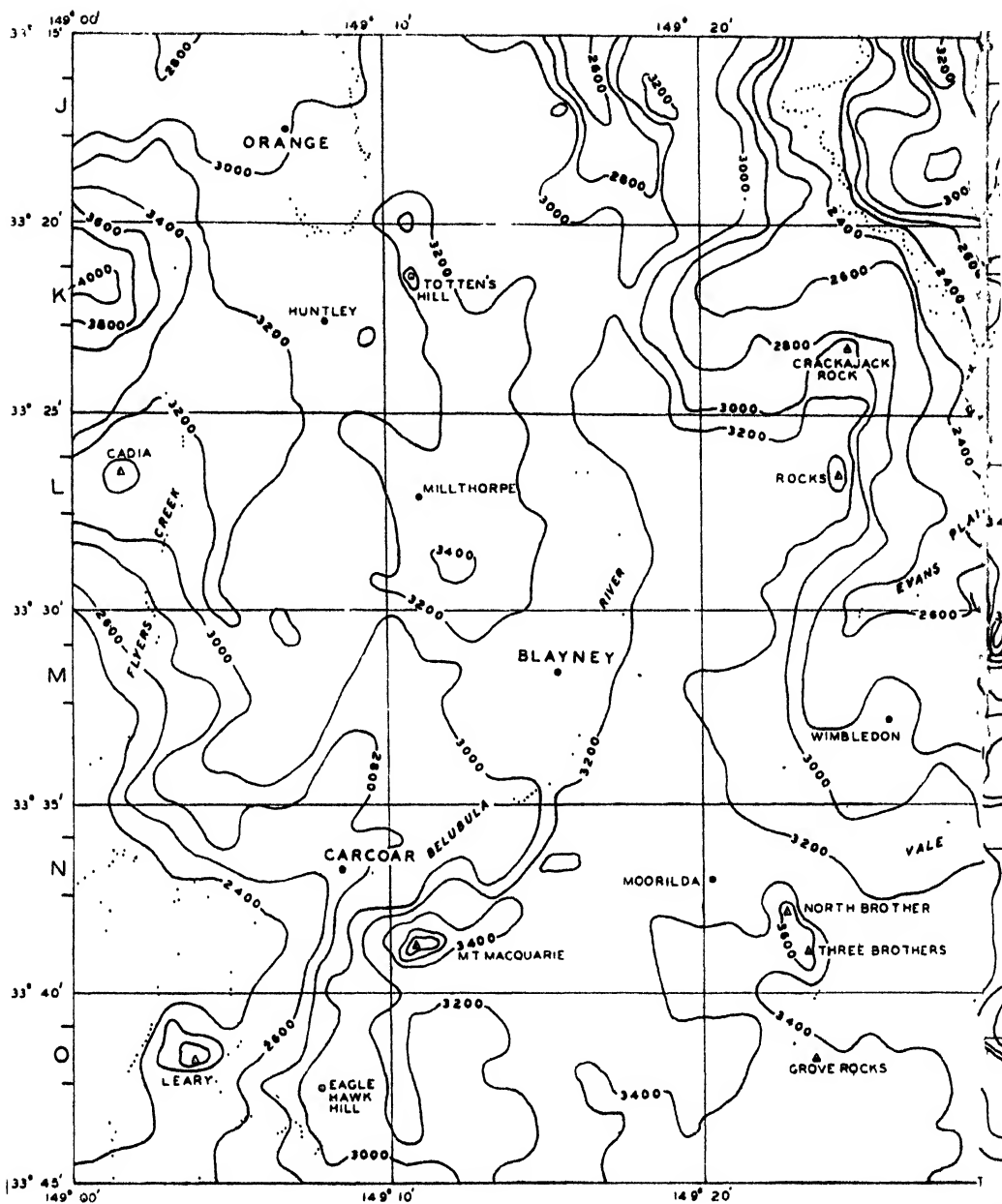
- (a) the accuracy and detail of the topographic data available,
- (b) the fineness of the mesh or number of "high point" observations per surface area, and
- (c) the nature of the topography.

The results of the altimetric frequency curves are of least value because as it has been shown the results vary with the choice and incidence of any given altitudinal unit. The other two methods are not subject to this factor and they have the added advantage that the personal element is minimised in their construction.

PART II. LANDFORM ANALYSIS OF THE ORANGE-BATHURST DISTRICT.

For the purpose of this study the Orange-Bathurst District is defined as that area surrounding the town of Orange and the city of Bathurst, bounded on the east by the Main Divide of New South Wales, on the west by the meridian

² Wooldridge and Morgan (1937, pp. 260-261), suggest a method which has a limited application.



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149° 00' E., and on the north and south by the parallels 33° 15' S. and 33° 45' S. respectively. (See Maps 1 and 2.) This area, of about 2,000 square miles, is drained by the Macquarie River and the Belubula River and their tributaries.

(1) Altimetric Frequency Curves for the Orange-Bathurst District.

In Figure 1, the frequency of occurrence of the heights of the "high points" in each 1,000 yards square on the topographic maps covering this area has been recorded. The frequencies have been plotted with the heights arranged as having an interval or range of 50 feet. For instance, heights recorded on the sheets of tracing paper as 2,800 are assumed to range between 2,800 and 2,850 feet.

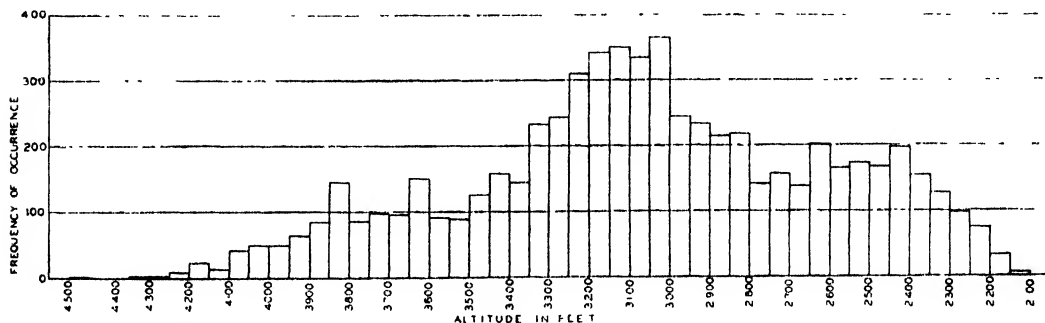


Figure 1.—Altimetric frequency curve for the Orange-Bathurst District.
Heights are grouped into ranges of 50 feet.

On this graph the range of 3,000 to 3,050 occurs most frequently in the area. Sharp drops in the curve indicating a preponderance of steep slopes occur at 2,800, 3,000 and 3,350 feet.

Attention may be drawn to several features of the curve.

(i) Between the values of 3,000 and 3,250 feet there exists a block of maximum frequencies which indicates an extensive gently sloping surface between these elevations, bounded particularly on its lower levels by steep slopes. (Maximum break in the curve occurs at the 3,000 feet frequency.)

(ii) Minor frequency maxima occurring at the 2,400-2,450, 2,600-2,650, 3,600-3,650 and 3,800-3,850 feet levels indicate local preponderance of surfaces at these levels.

(iii) Maximum breaks in the curve, in order of importance, occurring at the 3,000, 3,350, 2,800 and 3,250 feet levels may indicate that breaks of slope occur at these levels.

(iv) The curve decreases rapidly from a maximum at 3,000 feet to 2,650 feet; then it rises and the solid block of frequencies occurring between the 2,650 and 2,400 levels, bounded at each extreme by a maximum, indicates an extensive gently sloping surface between these elevations. The drop in the curve between 2,650 and 2,800 may indicate a steepening of the surface up to the 2,800 level.

(v) No attention can be paid to the frequencies for heights below 2,400 feet owing to the limited area in the Orange-Bathurst District at these lower elevations.

It is felt that the grouping of the frequencies for an altitudinal range of 50 feet is inadequate when dealing with any extensive erosion surface. On an ancient erosion surface it is almost certain that the range of height from its lowest point to its highest point and its local relative relief would in general exceed this.

On the assumption therefore that 100, 200 and 300 feet are more likely figures for the local relief of an erosion surface, the data were regrouped and frequency curves drawn. The 200 feet grouping, which is here presented in Figure 2, gave results which are more in accordance with the results from other methods and with field observations.

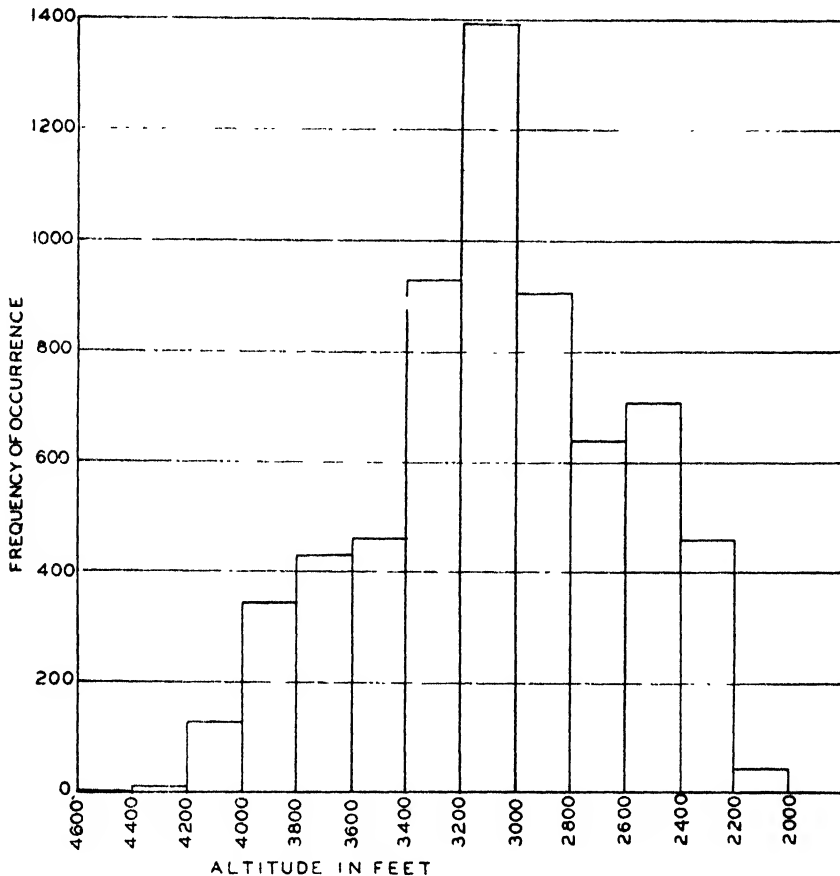


Figure 2.—Altimetric frequency curve for the Orange-Bathurst District.
Heights are grouped into ranges of 200 feet.

With this greater range, the frequency curve is naturally more striking. The range of heights from 3,000 to 3,200 feet occurs most frequently and is bounded on each side by a sharp drop in the frequency curve. Thus the dominant erosion surface in the region is one varying from a height of 3,000 to 3,200 feet above sea level. This surface stretches from Orange southwards through Blayney. Inspection of the topographic map shows that a considerable area of this surface is dissected to a depth of 1,000 feet. Other parts are reduced to a series of closely spaced, isolated hills, which diminish in altitude from south to north. This surface is portion of the Central Tableland of New South Wales and has been called the Orange Tableland. It would be more correct to refer to it as the Orange Plateau.

The next most important group on the graph is that of the frequencies for the range of heights from 2,400 to 2,800 feet. These two columns must be considered together for they are of almost equal value and they are bounded by sharp drops in the graph at 2,800 and 2,400 feet. The latter drop is accidental,

due to the artificial limits set down in defining the area. This 2,400 to 2,800 feet surface represents what is usually called the Bathurst Plains.

The graph suggests that a surface exists (Bathurst Plains) which has high points with an altitudinal range of 400 feet, while the preceding higher and more extensive surface (Orange Plateau) has a range of 200 feet only. This is borne out in Map 2, where these surfaces have been reconstructed. The "high-point" surface of the Orange Plateau is thus a smoother and more graded surface than the "high-point" surface of the Bathurst Plains.

The compact group of columns of approximately the same frequency value in the range from 3,400 to 4,000 feet may indicate a gently sloping surface within these altitudinal limits. The sharp break at the 4,000 feet value indicates the smaller number of areas over that height and is due to a number of residuals rising abruptly from the 4,000 feet surface to 4,400 feet.

(2) Strip "High-Point" Profiles for the Orange-Bathurst District.

In Figure 3, six strip high-point profiles running from west to east in the Orange-Bathurst District are presented. Map 2 shows the positions of these strips, each 3,000 yards wide and 10,000 yards apart from centre to centre.

The profile JJ, the most northern section, traverses two main surfaces, an extensive one at from 3,000 to 3,200 feet and another between 3,800 to 4,000 feet in the vicinity of Eskdale Trigonometrical Station. The break between the two surfaces is so abrupt as to suggest faulting or sharp warping. The 3,000 feet surface is cut by the gorge of the Macquarie River and by the wider valley of the Windburndale River. The level persists in the area between the two rivers and remnants of it are observed at the base of the steep rise to Eskdale.

In profile KK four surfaces are indicated. The lowest is the Macquarie Valley Plain, which is traversed by the channel and narrow flood plain of the Macquarie River. It has an elevation of 2,200 feet and is entrenched some 200 feet in the Bathurst Plains, which in the latitude of this profile have an elevation of from 2,400 to 2,500 feet. The most extensive surface is that at an elevation of 3,200 feet to the west of the Bathurst Plains. In the east the rise to the highest surface of 3,800 to 4,000 feet is very steep in the profile and on the ground surface. On this surface, residuals such as Sunny Corner Trigonometrical Station rise some 200 feet above its general level. At its western end the profile cuts the Canobolas Mountains, high residuals rising 800 feet above the surrounding district.

In profile LL the Orange Plateau is traversed at 3,200 feet and the remaining profiles show that this surface rises gradually to the south, where it attains a maximum elevation of 3,400 feet along the line OO. Some residuals such as North Brother, Middle Brother, Three Brothers and Mt. Macquarie stand some 200 to 300 feet above the general level. Along LL the Bathurst Plains are quite wide, and Panorama Hills, basalt-capped residuals to the west of the city of Bathurst, rise above the level of the surface.

In the region of profile MM the Bathurst Plains reach their widest extent and have a general elevation of 2,800 feet. Campbell's River and Fish River are entrenched some 300 feet into the surface; this corresponds with the entrenchment of the Macquarie Valley farther north. (See profile KK.) Profile NN runs to the south of the Bathurst Plains, where the valleys of Campbell's River and its tributaries have notched the 3,200 feet surface.

Profile OO does not exhibit the distinct breaks of slope indicated in the others. Instead the main feature is the long continuous upward slope of the upper surface from Eagle Hawk Hill through the Oberon Plateau to the Summit. This surface is broken by the valley of Campbell's River and between Oberon and the Summit by the Fish River Creek and Duckmaloi River.

The western border of the high eastern surface shows a remarkable change from north to south. In profiles JJ and KK it is very abrupt, in profile LL it is still steep but less abrupt. In profile MM a modification is introduced by the Fish River valley, but in profiles NN and OO the abrupt change has disappeared. This is particularly noticeable in profile OO, where the lower western surface, some 3,400 feet high, merges gradually into the higher surface at Oberon (3,800 feet) and the Summit (4,000).

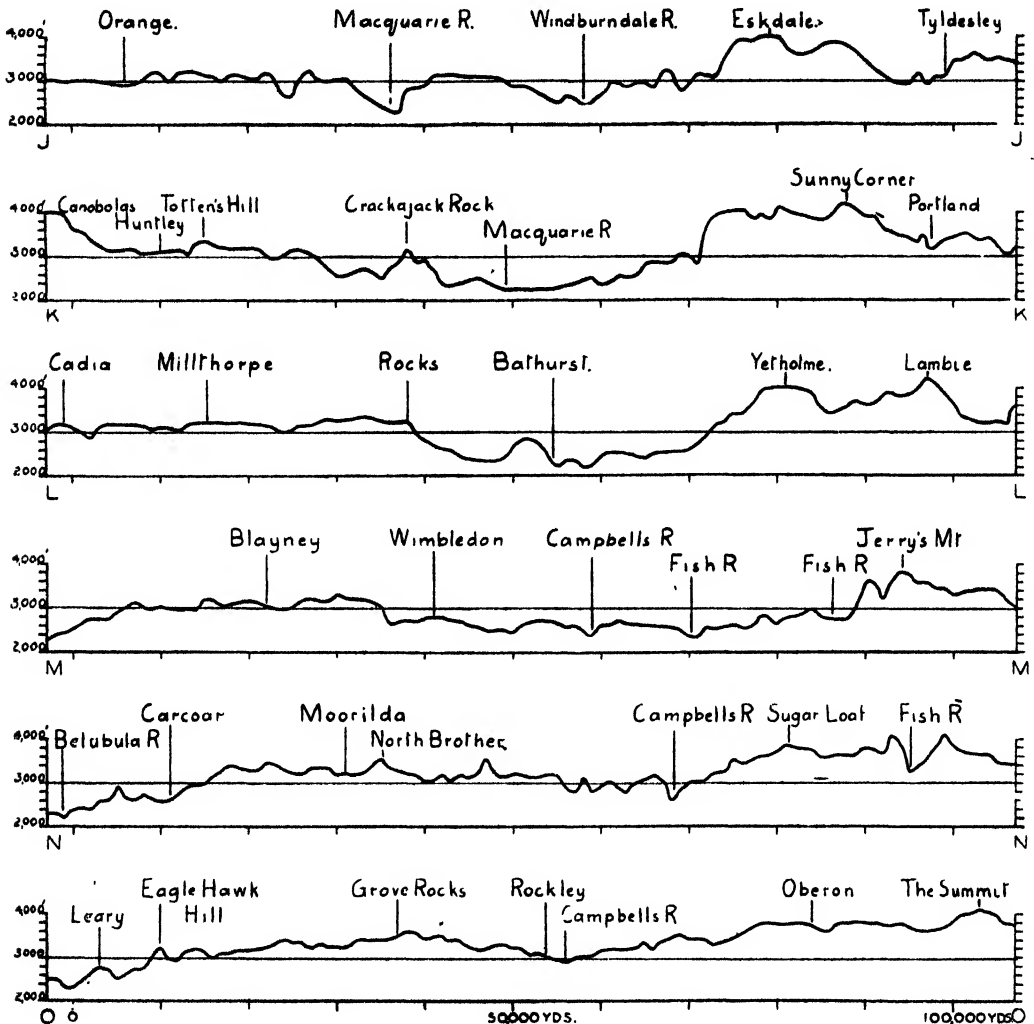


Fig. 3.—Strip "high-point" profiles for the Orange-Bathurst District.
The location of the strips is indicated in Map 2.

The strip high-point profiles thus illustrate the occurrence of the following surfaces :

- (1) The Eastern Surface or Yetholme Plateau, 3,800 to 4,000 feet, with some residuals (Sunny Corner, Mt. Lambie, etc.) rising to 4,200 feet.
- (2) The Orange Plateau, 3,000 to 3,400 feet, with some residuals (The Brothers, Canobolas Mts., etc.) rising some 200 feet above its general level. To the south this plateau seems to merge into the Oberon Plateau, at 3,800 feet.

(3) The Bathurst Plains, with an elevation of 2,400 to 2,800 feet.

(4) The Macquarie Valley Plain, elevation 2,200 feet.

The Yetholme Plateau and the Orange Plateau may be part of the same surface, the Oberon Plateau being the connecting link between them.

(3) Reconstructed or Generalised Contours for the Orange-Bathurst District.

In Map 2 the high-point surface of the Orange-Bathurst District has been reconstructed by using the high points in each of the 1,000 yards grid-squares as spot levels and drawing the contours at 200-foot vertical intervals.

The vast extent and even surface of the Orange Plateau extending from Orange southwards through Blayney is immediately apparent.

The detailed contour maps show that the amount of minor valley dissection has, particularly in the south-east corner, partly reduced this area to a number of isolated hills and the extent of the original summit surface is not nearly so apparent. This surface clearly extends to the east along the southern portion of the map at least as far as longitude $140^{\circ} 35'$. To the east of this the deep valleys of Campbell's River and Fish River isolate the Oberon Plateau (3,600-3,800 feet) from the Orange Plateau on the west and from the Yetholme Plateau surface on the east. But the spacing of the contours taken in conjunction with the profile OO in Figure 3 suggests that this was originally one continuous surface rising gradually from 3,200 to 3,800 feet and trenched by Campbell's River and the Fish River.

On this basis then it may be again argued that the Orange Plateau, the Oberon Plateau and the Yetholme Plateau were formerly one and the same surface. This surface was recognised by Andrews (1910) and is considered by him and other writers (Colditz, 1942) to be of Miocene age. The strip "high-point" profile and the generalised contours thus add further confirmation to the existence and continuity of the Miocene surface. In the south beyond the confines of the map the surface appears to be continuous and is clearly part of an east-to-west doming which produced the Blue Mountain Plateau surface. Passing north there may be faulting or a local increase in warping as suggested in profile JJ or KK.

The Bathurst Plains are also depicted in extent, and from the crowding of the contours at their margins it is obvious that the 2,800-foot line marks the upper limit in their development. They have apparently been excavated out of the Miocene surface and are probably of Pliocene age.

This surface has been described as a senkungsfeld by Sussmilch (1931), who suggests that the boundaries are determined by fault-planes. An examination of the contour map does not support the view that the northern, southern and western boundaries are fault-scarps, since, as shown by the contour lines, a number of long spurs project out from the upper surface. The western boundary is complicated by the basalt capped Panorama Hills which form a long spur between the Macquarie River and Evans Plains Creek. The latter and its numerous tributaries are actively besieging the Orange Plateau along a steep slope which is almost continuous with and similar to the slopes forming the deep entrenchment of the lower course of the Macquarie River. The reasons for the steep breaks of slope which occur in various places bounding the Bathurst Plains may be assigned either to faulting or to changes in rock character. No detailed geological maps of this area have been published, but David (1931) and Sussmilch (1931) both indicate that there is a considerable variation in rock character within the area. The Bathurst Plains have been mainly cut in granite. The Orange Plateau is in part covered with Tertiary basalt overlying highly inclined Ordovician and Silurian strata. In the Yetholme Plateau there are areas of granite and Lower Palaeozoic strata of Silurian and Devonian age. In

conversation, Mr. L. L. Waterhouse, who has carried out geological surveys in this area, stresses the fact that the varying resistance to erosion of the rock types has played a very important part in determining the extent and shape of the major and minor landform features. It also is necessary (Bryan, 1940) to bear in mind the possibility that during retreat caused by erosion, the slopes bounding the Bathurst Plains have maintained their steepness. In regard to this Davis (1932) has laid it down that slopes flatten during the progress of the cycle of erosion, whereas Penck (1924) maintains that slopes retreat without loss of their inclination and that steepness disappears only because the land above the grade of the gentle slopes has been consumed.

If Penck's view is correct, and experience would indicate that it is more feasible and acceptable than that of Davis, then once a surface experiences an initial entrenchment, when steep slopes are formed, these will persist in their inclination as they retreat, exposing the new and lower erosion surface. Normal retreat through erosion, then, rather than faulting, may be the cause of the steep slopes bounding the Bathurst Plains. Thus the Bathurst Plains, if eroded out of a higher surface which has not been completely consumed, should be bounded by slopes which in general would exhibit the degree of steepness of the original entrenchment.

The slopes to the north, west and south of the Bathurst Plains are only a slightly more gentle version of the slopes of the gorge of the lower part of the Macquarie River shown on the map. These latter slopes have been oversteepened with the new phase of erosion which initiated the cutting of the Macquarie Valley Plain out of the Bathurst Plains. Even in this case the break from the Bathurst Plains to the Macquarie Valley Plain is quite steep, though of small magnitude.

The eastern boundary of the Bathurst Plains has been referred to in the previous section. The upper steepness which may be due to faulting, warping or differential erosion has been accentuated by the retreat of the erosion slope almost to its base. The map and the strip profiles show that there are a few remnants of the 3,200 feet surface along the bottom of the steep upper scarp.

The Eastern or Yetholme Plateau surface can be seen in Map 2 to vary in height from 3,800 to 4,000 feet with small residuals of an older surface rising up to 4,200 feet. It is also interesting to note that in both Map 2 and in Figure 3, the Main Divide, separating the eastward from the westward flowing rivers, does not correspond with the "high-point" line; it is invariably to the east and is much lower.

SUMMARY.

Three methods of landform analysis which can be rigidly and consistently applied to topographic maps have been described. Using these methods, one can set down with some precision facts about the various summit planes which are not at all obvious from mere inspection of the contour map. These methods have been applied to the topographic maps of the Orange-Bathurst District, New South Wales. It has been shown that at least four separate erosion surfaces exist and the map depicts their nature and extent.

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THE RELATIONSHIP OF THE AUSTRALIAN CONTINENT TO THE PACIFIC OCEAN—NOW AND IN THE PAST.*

By W. H. BRYAN, M.C., D.Sc.

INTRODUCTION.

I feel singularly honoured at having been invited to give the Clarke Memorial Lecture for 1944. It is an honour to be chosen for the task of commemorating such a worthy scientist and pioneer as William Branwhite Clarke, and it is an added honour to be admitted to the select company of those who have given the lecture in the past.

Although Clarke is best known for his geological work in the State of New South Wales, he also played a very important part in laying the foundations of the geology of Queensland. Indeed during the earlier part of his career, that is until 1859, he was employed by the Government of New South Wales in what was then called the Northern District, which included the present State of Queensland. Clarke did not make many visits to this, the northernmost part of his field, but he made most valuable use of his occasional excursions. The extent of his influence on our northern State is best seen not in his own writings, but in the well-known book on *The Geology and Palæontology of Queensland* as set out by R. L. Jack and R. Etheridge, Jr., in 1892. This great and enduring work, which was published in 1892, is dedicated "to the memory of three worthy pioneers in Australian Geology, Samuel Stutchbury, William Branwhite Clarke and Richard Daintree". The book itself shows clearly why Clarke was one of the three men so honoured. The text will be found to contain nearly sixty references to his work, and these are not clustered about a few points, but find a place in almost every one of the forty chapters that constitute the book.

As a Queenslander and as a geologist, I am glad to acknowledge the extent of our indebtedness to the great man whom we commemorate this evening.

THE PACIFIC AT PRESENT.

The most striking feature of the Pacific Ocean is, of course, its immensity. It covers more than one-third of the globe; it occupies a greater area than all the continents put together; it is far larger than any of the other oceans. But although the absolute size of the Pacific is impressive, and may be of the first importance as bearing on its mode of origin, and although its size relative to the other major geographical units is of undoubted interest, these quantitative considerations may not be as significant as those qualitative features that are distinctive of and, in part, peculiar to this ocean. The differences of degree that separate the Pacific from the other major units are important, the differences of kind may well be fundamental.

Certain obvious geographical features of the Pacific Ocean as depicted on a terrestrial globe at once attract the attention of even the casual observer. Perhaps the most striking of these is that it occupies a basin almost completely surrounded by land. This is clearly seen on any globe, and on those maps based

* Clarke Memorial Lecture delivered before the Royal Society of New South Wales, May 30, 1944.

on appropriate projections. Unfortunately, the world maps on Mercator's and similar projections so commonly in use distort the higher latitudes so much that the principal gap in the encircling land masses (that of 1,500 miles or so which separates New Zealand from Antarctica) looks far greater than it is. This misleading effect is further emphasised owing to the custom of curtailing in many of these maps the higher latitudes of the southern hemisphere (although the same maps include the corresponding latitudes in the northern hemisphere). In this way the large continent of Antarctica is frequently omitted altogether and the Pacific basin wrongly appears to have a huge opening in the south.

A second distinctive feature of the Pacific is the close parallelism between the coast line and the adjacent mountain ranges of its eastern margin, which persists almost unbroken along the whole western coast of the Americas.

Another striking pattern is to be seen on the western side of the Pacific where a series of outlying island arcs is linked together to form a chain extending down the whole length of the Asiatic coast.

Simple observations such as these have probably been made by innumerable school children, generation after generation, but their obviousness does not detract from their significance, and they form the basis of the more elaborate generalisations that have been put forward by trained geographers from time to time. Of these, one of the earliest and most important appears to have been that of von Drasche (1879, p. 265), who recognised that the island arcs of Asia, in spite of their distinctive pattern and outlying position, were to be regarded as homologous with the mountainous coasts of the American mainland, and who therefore suggested that the western boundary of the Pacific Ocean proper should be drawn, not along the coast of the Asiatic mainland, but from Kamschatka through Japan, the Philippines, to New Guinea, on to New Caledonia and New Zealand and thence to South Victoria Land in Antarctica.

Six years later Suess (1885, Vol. 1, p. 5) argued that the various coasts of the Pacific Ocean, although they might differ in detail, all conformed to the one geographical plan in that they all exhibited a close parallelism between the shorelines and the direction of the neighbouring mountain chains. Although he did not suggest that coasts of this description were restricted to the Pacific, Suess pointed out that they were so characteristic of it and so different from the coasts of the other oceans as to warrant the term Pacific Type. In contrast, the coasts which exhibited no parallelism between the shore lines and the nearest mountain chains he referred to as the Atlantic Type. The geographical differences between these two coast types, it is important to note, are differences of kind not merely differences of degree, for whereas the Pacific Type is defined on the basis of a positive criterion the Atlantic Type is based only on negative or at best neutral criteria.

The geographical elements of the Pacific margin are indeed in such close harmony as fully to merit the term "Concordant Coasts" afterwards introduced by Supan (1911, p. 793). On the other hand the lack of relationship between the geographical and geological features of the Atlantic coasts equally merits the term "discordant".

Suess was the first to emphasise that the geographical homogeneity of the Pacific coasts has a geological basis. Earlier workers doubtless anticipated his reference to the important and significant facts that the Pacific margin was paralleled by a volcanic zone—the so-called "Girdle of Fire" and a similarly placed seismic zone, where earthquakes were frequent and severe, but Suess made important additions to these well-known generalisations. Thus he pointed out that the bordering mountain ranges are all folded towards the ocean and that a Mesozoic marine series can be traced around the Pacific.

J. W. Gregory (1913, p. 41), while in general agreement with Suess' generalisations, elaborated and strengthened them by his constructive criticism. In

particular he showed that even where the Pacific type of coast was represented by outlying island arcs, the coast of the mainland itself, although very different, was in harmony with Suess' general plan. Gregory demonstrated this by subdividing the Pacific coast types into Primary Pacific Coasts which "are determined by the proximity of long lines of fold mountains, to the trend of which the coast is in general parallel. The mountains bounding these coasts are of comparatively young geological age. Over-thrusts and over-folds, if present, are mostly directed toward the ocean", and Secondary Pacific coasts that "are due to the subsidence of basins on the inner side of mountain chains along coasts of the Primary Pacific type. They are frequently bordered by active or recent volcanoes. The oldest rocks usually occur along the coast and are followed by younger rocks further inland. Except where horsts project into the sea, the coast-line is approximately parallel to the average grain of the adjacent country." In his Primary Pacific coasts Gregory included the Asiatic arcs together with Taiwan, the Philippines, New Guinea, New Caledonia and New Zealand, while the eastern coast of Asia proper and that of Australia were referred to his Secondary Pacific coasts. Gregory was further of the opinion that both of his Pacific coastal types were represented in Antarctica.

As a result of this work Gregory went far to establish the geographical and geological unity of the Pacific as it at present exists, although, as we shall see, he was strongly opposed to the idea of the Pacific Ocean as a permanent feature of the earth's crust.

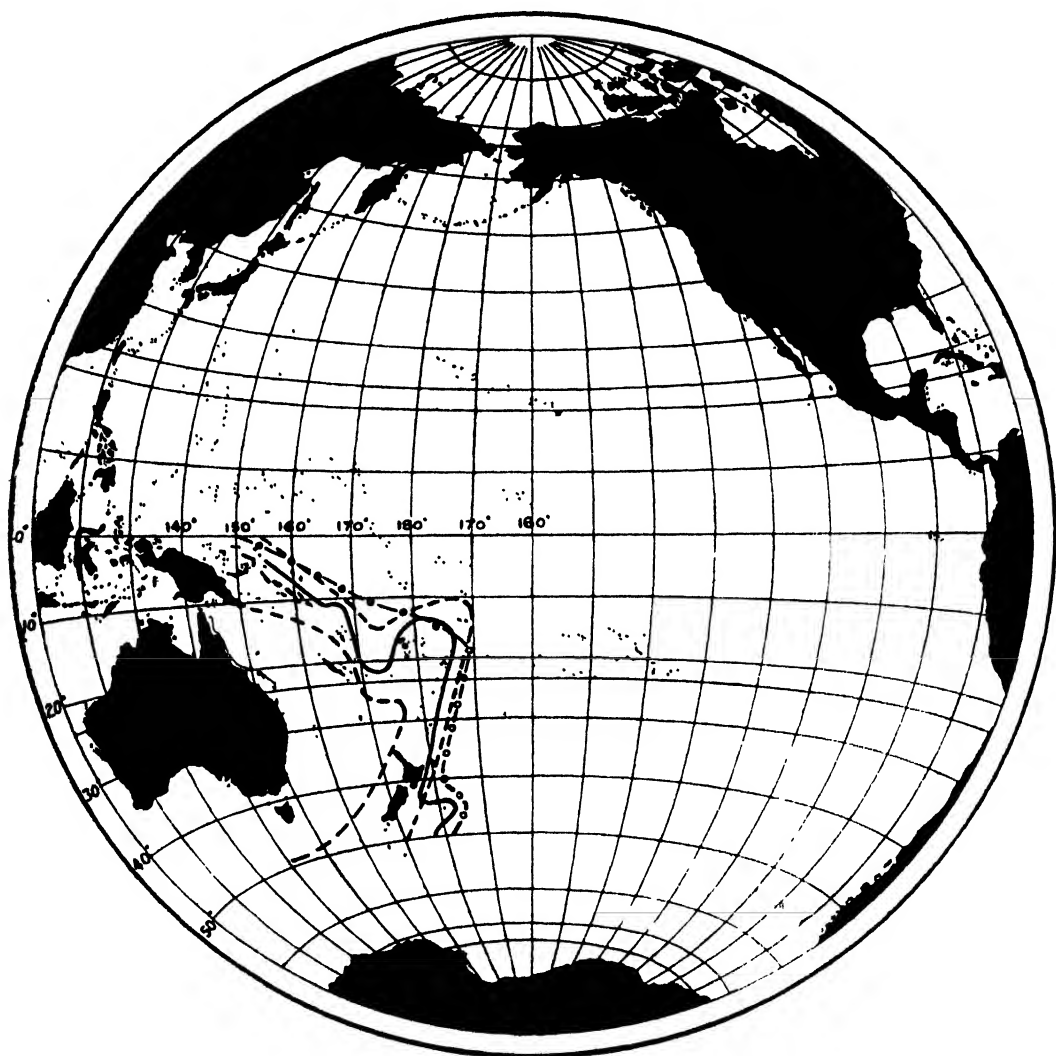
Most subsequent workers have been in general agreement with Suess' views as interpreted by Gregory, for they are based simply on facts of distribution, but from time to time modifications have been suggested as new knowledge has been gained or as some new avenue of approach to the problem has been discovered. Of the more strictly geographical additions two may be selected for reference—Marshall (1911, p. 99) urged the replacement of the New Guinea, New Caledonia, New Zealand margin by another that included the Fiji, Tonga and Kermadec islands; and Taylor (1928, p. 995), while agreeing as to the importance of the Asiatic island arcs as usually defined, pointed out that the less conspicuous but very large Mariana arc although "new and weak in its development" must be taken into consideration as a likely alternative for the true edge of the Pacific basin south of Japan.

Of the geological contributions that have provided supplementary evidence of the unity of the Pacific, the most interesting was perhaps that of Becke (1903, p. 125), who pointed out that, whereas the volcanoes circling the Pacific were predominantly andesitic—we may remind ourselves that the very name of the rock andesite is based on its common occurrence in the Andes—the volcanoes of the extra-Pacific regions are characterised by the alkaline basalt, tephrite. Of this important generalisation Suess (Vol. IV, p. 588) wrote: "Thus there is a tephritic or Atlantic series, and an andesitic or Pacific series. The Atlantic series is characterised by the greater quantity of alkalis, especially sodium, while in the Pacific series the alkalis diminish and calcium and magnesium occur in greater quantity." He added that "All the coasts of the Pacific Ocean—from New Zealand to Java, Alaska and all the western coast of America belong to the andesitic series". Becke had also pointed out that the Pacific type volcanic rocks were associated with folding movements while those of the Atlantic type were related to faults.

Harker (1909, p. 90), who had been working along similar lines for many years, brought forward a comparable but even more comprehensive scheme of distribution, which was not confined to volcanic rocks or to recent geological times. In this he divided the igneous rocks of the world into two great groups, which he named the "Atlantic suite" and the "Pacific suite" respectively on account of their segregation into two great petrographical provinces arranged

in and about these oceans. The Atlantic suite was characterised by alkaline rocks and the Pacific by calc-alkaline. Furthermore the Atlantic and Pacific suites were associated with structures due to tension and to compression respectively.

The next advance along these lines was made by Born (1933, p. 759), who concentrated on the geographical relationship of the andesitic lavas characteristic



AUSTRALIA'S PLACE IN THE PACIFIC.

- The Marshall Line.
- - - Born's Andesite Line.
- The Limits of the Seismic Belt.

of the circum-Pacific lands to that of the basalts characteristic of the Pacific itself. He argued that the line of demarcation, "the Andesite Line", was, in the western Pacific, only in partial accordance with the edge of the basin as defined by von Drasche, Suess and Gregory, for it followed the Mariana arc in the north and the Marshall Line in the south, thus giving strong support to these important modifications of the original plan.

The most recent contributions to our knowledge of the nature and limits of the Pacific basin are based on seismological observations. These have recently been summarised by Gutenberg and Richter (1941) in their most informative "Seismicity of the Earth".

Although the earlier views with regard to the distribution of earthquakes gave strong support to the claim of Suess that the Pacific basin was a structural unit, the support was only of a general kind. Thus it was known that the great majority of earthquakes, especially the large ones, occurred within a circum-Pacific belt, but the belt was not clearly defined and appeared to include some quite large areas within the Pacific basin proper.

The result of Gutenberg and Richter's work has been to give far more specific and even more convincing support to the hypothesis that the Pacific is not only a homogeneous unit but differs qualitatively from all the other major geographical units, continents and oceans alike. Their principal conclusions with regard to the circum-Pacific belt may be summarised as follows: (1) it includes a large majority of the (common) shallow shocks with epicentral depths of less than 30 kilometres. (2) It contains a still larger proportion of the intermediate shocks from depths between 30 and 300 kilometres. (3) It contains *all* the shocks from a depth greater than 300 kilometres. (4) It separates areas of continental structure from those of Pacific structure. (5) It surrounds an area (the Pacific basin proper) which is "conspicuously inactive".

The circum-Pacific seismic belt as now defined is of sufficient precision to afford definite information on two debatable sections of the margin of the basin. Thus to the south of Japan the belt is quite clearly split into two branches, one of which follows the inner island arcs adjacent to the Asiatic mainland (the edge of the basin as suggested by von Drasche), the other following the festoon of the Mariana arc and agreeing nicely with the position of the Andesite line as drawn by Born. But the belt to the south-east of New Guinea follows only the outer of the two suggested margins and thus lies beyond New Caledonia and follows the Marshall Line very closely.

Attention may be directed particularly to the deep earthquakes listed by Gutenberg and Richter, which total no fewer than 212. Although the origin of these is still in dispute, there is general agreement as to their significance as indicators of deep-seated instability. Writing on the "Structure of the Pacific Basin as indicated by Earthquakes" Gutenberg (1939) stated: "The fact that the foci of all earthquakes originating deeper than 200 miles have been found close to and on the continental side of this [circum-Pacific] boundary indicates that the Pacific Basin has a unique structure." This all-important conclusion Gutenberg supports by another line of evidence, namely the peculiar nature of the sea floor under the Pacific. Reviewing Suess' well-known suggestion that the floors of *all* the oceans are composed of *sima* (as contrasted with the *sial* of the continents), he has concluded from a study of earthquake travel times under the several continents and oceans that "the surface structures of the Atlantic and Indian Oceans are similar to those under the continents but thinner . . ." whereas "All evidence agrees with the conclusion that the layers which form the uppermost crust in the continents are lacking in the Pacific Basin . . ."

This restriction of *sima* to the floor of the Pacific, while it introduces an important modification to what was probably the most famous of Suess' generalisations, is nevertheless quite in accord with the spirit of that genius who never tired of emphasising the essential differences of origin, history and structure that separated the Pacific and Atlantic oceans. Gutenberg's contribution represents an advance rather than a conflict, and one feels sure that Suess would have welcomed it as such.

The evidence converging from many points has now reached such impressive proportions and is so clearly interlocked and mutually confirmatory that the

present unity of the Pacific basin is now accepted by the great majority of geologists, although not all of these may yet be convinced as to its uniqueness.

THE PACIFIC IN THE PAST.

If we agree to accept the unity of the Pacific as sufficiently well established, our next step should be to determine, in so far as this can be done, how long it has existed as a unit.

It is patent that its unity was not achieved in recent geological times. The ring of volcanoes which circumscribe the basin are not all active. Many are dormant and others appear to have been extinct for very considerable periods. The mountains that circle the Pacific are due to folding movements which, although confined to the Cainozoic, may well have been initiated very early in that era. Further, many geologists holding quite diverse views with regard to the structure and history of the Pacific basin have been impressed by the evidence on which Haug based his generalisation for a continuous Mesozoic sea, the position of which was in close harmony with the present margins of the basin, although few of them follow Haug in his conclusion that the site of the Pacific was then occupied by a great continental mass. The most recent reference to Haug's Mesozoic "geosyncline" is that of Wade (1941), who in his paper on "The Geology of the Antarctic Continent and its Relationship to Neighbouring Land Areas" wrote that "there can be little doubt that the Andean geosyncline is continued by way of the great loop to Graham Land and crosses the Antarctic Continent through James W. Ellsworth and Maria Byrd Lands. Nor can there be any doubt that the geosyncline passing through New Zealand also connects on the opposite side of the continent to Graham Land and is part of the same circum-Pacific geosyncline."

Back beyond the Mesozoic era there seems to be little direct evidence either for or against the existence of the Pacific basin as such.

It is not the intention here to canvass the detailed evidence for and against the permanence of ocean basins, but the following points may be emphasised.

Dana, the original protagonist of the theory, placed all the oceans in the one category and argued that they were all essentially permanent features of the earth's crust.

Suess adopted a different attitude and consistently emphasised the contrasts between the Atlantic and Pacific Oceans, claiming that they were different in structure, history and origin, and that the Pacific was the older and more permanent feature. Suess' claim has been strongly fortified by recent seismological advances which indicate that the Pacific is even more fundamentally different from the Atlantic than he himself had supposed.

J. W. Gregory, although he was largely responsible for demonstrating the present unity of the Pacific, remained unchanged in his early belief that all the ocean basins belonged to the same category and that none was permanent. He argued as vigorously and confidently against the permanence of the Pacific in 1930 as he had against that of the Atlantic in 1929. Further he expressed the opinion that the Pacific might even be the youngest of the oceans.

The permanence of the Pacific throughout geological time is far from established, but its assumption as a working hypothesis is, I think, warranted for the following reasons: if, as the recent evidence suggests, the Pacific basin is a unique structure, its origin may well have been due to some special event or circumstance early in the earth's history, that may not have been directly relevant to the origin of the other oceans. But even if this be not admitted and the Pacific be retained in the same category as the other oceans, every argument of a general nature in support of the permanence of ocean basins can be applied with special cogency to the Pacific, while general arguments against permanence are weaker when applied to that ocean than to others.

If, then, we assume that the enormous Pacific basin has been a permanent feature on the earth's surface, its effects, both direct and indirect, on the history of the earth must have been prodigious. For, in the first place, its birth may well have been due to some earth-shaking event, the repercussions of which have come echoing down the ages. But even if its origin were unaccompanied by any such dramatic circumstance, the very presence of such a large and permanent structure would doubtless have had far-reaching and long-lasting effects upon the course of geological history.

But, this evening, we are concerned not so much with these general considerations as more particularly with the implications on the structural and stratigraphical history of the Australian continent, of the permanent presence of such a powerful neighbour.

Let us then change our point of view and now look at the Pacific Ocean from our Australian vantage point.

AUSTRALIA AT PRESENT.

The Australian continent as it exists at present is by far the smallest of the major land areas and appears almost insignificant beside the mighty Eurasian continent to the north. It is small even compared with Antarctica, which is half as large again. And if we consider relative masses instead of areas Australia becomes even less impressive on account of its low average height—far smaller in bulk than any of the other continents, and only one-twelfth that of Antarctica. Indeed, as a continent, whether we consider its area or mass, Australia seems quite out of scale.

On every side Australia appears to be geographically incomplete, but our present interest is with that part fronting the Pacific. Here, quite clearly, the minor topographical features of the land surface can be traced beneath the Pacific. This may be simply explained as due to a submergence of the coast of only two hundred feet or so. But many major geographical features also appear to be truncated at the coast line and something far more important than a relatively small change in sea level is indicated.

Geologically, the incompleteness of Australia is even more marked. It reminds one of a damaged picture in which so much has been torn away that the composition of the remainder, incomplete and out of balance, leaves us wondering what the picture as a whole looked like.

It is of especial interest that the first scientist to realise the geological incompleteness of Australia was the man in whose honour we are assembled this evening and whose discernment in this as in other geological matters was unusually acute. Clarke (1878, p. 7), basing his conclusions on the complete absence of marine strata of Tertiary age from the eastern coast of Australia, suggested that a former extension has been lost by subsidence into the Pacific. He added that "this has some support in the fact that there is a repetition of the Australian formations in the Louisiade Archipelago, New Caledonia and New Zealand—in the latter of which occur abundant Tertiary deposits".

The present coast line has, at most, only a secondary significance, in that, instead of forming the natural limit to the geological structure, it merely reflects the general geological grain. We have seen that Gregory could not agree with Suess that the coast of Australia proper was comparable with the more typical coasts of the Pacific, and placed it with his Secondary Pacific coasts which in no case indicate the true limit of the land. They are essentially coasts developed within a coast.

Some geographers, including Sir John Murray, emphasise the importance of the 100-fathom line as probably representing the edge of the continent proper. In Queensland the outer edge of the Great Barrier Reefs virtually coincides with this line for a good part of its length and thus gives it added emphasis. Some years ago (1928), using as my basal assumption that the 100-fathom line

represents the common limit of continental masses, I endeavoured to explain the variable breadth and strangely convex projection of the Queensland continental shelf as a natural extension to the east. In view of the fact that the eastern edge of the continental shelf and the western edge of the highlands are symmetrical about the coastal ranges of Queensland, I suggested the hypothesis that the continental shelf represents the drowned half of the Queensland highlands of which the coast ranges formed the dominant axis. A consideration of the structural geology of Queensland appeared to support the hypothesis, for the known highlands are composed of Palæozoic rocks laid down in a geosyncline, the supposed eastern edge of which roughly coincided with the edge of the continental shelf.

Spender (1930, p. 279), commenting on this suggestion, expressed the opinion that I had not gone far enough, and that at least for a considerable part of the Queensland coast the 100-fathom line does not mark the eastward limit of the continental mass since "from Saumaurez Reefs in lat. 22° S. . . . to Osprey Reef in lat. 14° S. . . . there is a great bank within the 1,000-fathom contour".

Extending our observations still further to the east we note that the now isolated island of New Caledonia has all the appearance of being an outlier of the main Australian mass. It fits perfectly into the geological picture. In 1925, after pointing out that in addition to the more conspicuous geological trend to the north-north-west, Queensland rocks also exhibited an older trend to the north-east, I wrote that "it is a notable and probably significant fact that the north-east trend is most strongly developed in that part of Queensland adjacent to the abnormally wide portion of the continental shelf which is here projected in a north-easterly direction. It is also known that parallel north-easterly trend lines actually pass through New Caledonia. The presence of these north-easterly trends in the old metamorphics of this island (in which all the newer rocks trend N.N.W.), which Suess regarded as one of the three most puzzling features of the Melanesian arcs, is thus simply explained if New Caledonia be regarded as part of an ancient Australian continent."

Most Australian geologists would, I think, be in agreement with Jensen's (1936) statement that "the island of New Caledonia is a remnant of a once continuous continent, the Melanesian plateau, which extended westwards to eastern Australia and New Guinea, and south perhaps to New Zealand".

But New Caledonia does not necessarily mark or even approximate the eastern edge of the Australian structure, as Woolnough (1903) showed us over forty years ago when he described from Fiji rocks of ancient aspect which he concluded might well be Archæan in age, and which indicated that the Fiji Islands instead of being a cluster of oceanic islands were remnants of a continental mass that once extended eastwards from Australia.

With regard to the true limit of the Australasian mass, the most satisfactory statement and one for which Australian geologists are particularly indebted is that of Marshall (1911), who in his reasoned and critical address to the Australasian Association for the Advancement of Science, concluded that :

- "1. Bathymetrical, structural and petrographic characteristics support the idea that the real boundary of the south-west Pacific passes through New Zealand, Kermadec, Tonga, Fiji, New Hebrides, Solomon and on to the Admiralty Islands.
2. That this practically coincides with biological knowledge as to plant and animal distribution within the area.
3. That the land connection or approximation took place in the late Mesozoic or in the Pleistocene, probably in both.
4. That the eastern Pacific islands are different in structure, nature and origin from the lands on the line of islands mentioned, and that they have derived their fauna and flora by chance migrants from them."

Marshall added that "it is perhaps necessary to explain what one means by the statement that the island line so often referred to is the real margin of the Pacific basin. By this statement it is intended to convey the meaning that any movement of elevation or depression, or any rock movements that may have affected that portion of the earth's crust that lies to the west of this line, may have left all that which lies to the east unaffected. In other words, the structural margin is supposed to mark the limit of that portion of the area that according to geological ideas may in the past have formed an eastern extension of the Australian continent."

The marginal line as thus defined has frequently been mentioned with approval in geological literature.¹ Indeed it is most striking to observe how geologists of almost every creed are unanimous in accepting the fact of the Marshall Line, although they may disagree fundamentally as to its implications. Thus while Schuchert regarded it as marking the limit of a vigorous continent at the acme of its development, T. C. Chamberlin (1916) thought of it as the boundary of an abortive mass that had failed to achieve the status of a continent proper.

Let us consider the significance of the Marshall Line as it affects Australian geology.

There is a tendency, seldom stated explicitly but frequently implied, to regard the present Australian continent as intact, complete and sufficient to itself—a perfect example of geological autarchy! If the submerged outlying portions are taken into consideration at all they are regarded merely as the unstable margin of a stable continent—the rickety front porch of an otherwise well constructed house. Let us make an inspection of this front porch. First, let us measure its dimensions. It reaches to Tonga 2,000 miles from the nearest point of our present coast. Its area is approximately three million square miles, that is about equal to that part of the Australian mass now above sea level. It is certainly a large porch.

Now let us consider its stability as compared with the rest of the house. The only satisfactory criterion for comparing the stability of neighbouring areas as they exist today is that of seismology, and this shows quite clearly that at the present time there is a seismic zone developed on either side of the Marshall Line within which seismic disturbances are frequent and severe, but the area between the inner edge of this seismic belt and the present coast of Australia, far from being rickety, is every bit as stable as Australia itself. To take a specific example, New Caledonia is, judged by the criterion of seismicity, as stable as central Australia. During the past seven years I have carefully scrutinised every record obtained by the Seismological Station of the University of Queensland in my search for evidence of earthquakes between the Australian coast and the Marshall Line. Earthquakes on or near the Marshall Line itself are of almost daily occurrence, but they never occur within the magic circle of the seismic zone. I have watched particularly for disturbances, even small ones, from the edge of the Great Barrier Reef, which especially might be expected to yield evidence of mobility, but although our station is in an excellent position for receiving such shocks, not one has been recorded. One cannot avoid the conclusion that one large continuous stable mass now extends almost to the edge of the Pacific basin proper, which is also an essentially stable area. The Marshall Line thus shows up all the more vividly as the mobile hinge between two great stable masses.

Recently, investigations have begun in our seismological station with a view to determining the nature and thickness of the material composing the

¹ As a tribute to an eminent geologist I have referred to it in this lecture as the Marshall Line.

Australasian mass. The results of this are far from complete, but the first indications, as calculated by my assistant, Mr. N. de Jersey, are that Australia proper consists of sial to a depth of approximately 40 kilometres, and is in this respect closely comparable with western North America, while the area between the Kermadec and the present Australian coast also consists of sial, but in a much thinner layer of about 25 kilometres, and thus comparable with Gutenberg's findings for the floor of the Atlantic. This suggested difference in thickness as between the emergent and submerged portions of the continent, important though it may be, does not appear to have any effect on the present stability of the submerged part whatever it may suggest with regard to its mobility in the past.

We may, I think, reasonably conclude that the alleged rickety front porch is in fact a large and important part of the house proper and that it is as firm as the remainder.

The Australian continent of the geographers is, we may conclude, not, as commonly believed, a geological unit. It is not an integer, it is a fraction. With the frank recognition of this we should abandon the geological isolationism that characterises so much of our work, and seek to understand the position of Australia in the general scheme of things and, more particularly, of the part it plays as one of the circum-Pacific continental masses.

AUSTRALIA IN THE PAST.

We might well begin with a consideration of the most appropriate cartographical basis on which to place the various interpretations of the growth of our continent. It is customary at present to study the past history and geography of Australia with reference to its present geographical outline. This has certain obvious advantages, the chief of which is that we are referring that which is doubtful to that which is certain. But these are offset by equally marked disadvantages attached to the method. The uniformitarian dictum that "the present is the key to the past" is irrefutable in as far as it means that the known is the key to the unknown, but in as much as it suggests that the present is to be regarded as the normal state of affairs it is highly dangerous. Dr. Woolnough has consistently and with good reason warned Australian geologists against using present day conditions as a measuring stick for the events of the past. The present geographical outline of Australia does not represent the norm, and therefore should not be used as our standard of reference. To a geologist, looking at a map of Australia is like viewing the last picture of an incomplete cinematograph film. Viewed as a "still" it has all the appearance of permanency, but seen as an episode in the geological story of Australia it is merely a transitory flick. The present geographical outline is neither normal nor permanent: nor does it represent a culmination. It is a point arrived at, not a goal achieved.

The question thus arises, is there any better basis for a palæogeographic map than the present continental outline? I suggest that the most logical background available for all but the Upper Tertiary maps is the area limited by the Marshall Line. It is not likely that this line has been rigidly fixed throughout our geological history, but even so, it is likely to be a more significant datum than the present transient coast line. The suggestion is not strictly original for, thirty years ago, my old friend and teacher, Dr. A. B. Walkom (1919) set us all a good example by publishing with his Mesozoic maps of the Australasian region a reference map showing the "approximate limits of the Continental Mass, of which Australia, New Zealand, New Caledonia, etc., are remnants". Perhaps a satisfactory compromise with present practice could be effected if our palæogeographic maps showed both the Marshall Line and the present coastal outline, the former to indicate the distribution of land and water within the

Australasian mass, the latter for ease of geographical reference. In this way our convenience might be served and at the same time our perspective retained.

I propose that we now consider the history of our continent in terms of the great Australasian mass noting, at the same time, how this history fits into the picture and story of a permanent Pacific.

It would be convenient for our purpose if we could make use of some generally approved summary of the geological evolution of Australia, in which controversial details disappeared into a background of generalisations acceptable to all. Unfortunately, no such general statement is possible, for Australian geologists are as strongly at variance in their interpretations of the major aspects of our geological history as they are about the significance of stratigraphical details.

If, instead of completely accepting any particular viewpoint, we endeavour to amalgamate the principal features of the several schools of thought, we are confronted at the very outset by an impasse, for Australian geologists have long been in sharp disagreement as to the nature of the pre-Cambrian "foundation block" on which all our geological history is based. On the one hand are those who regard it as representing the minimum development of our continent, and on the other are those who picture it as marking the maximum! And even if we evade this initial obstacle by beginning our history with the Palæozoic era, we are left with the impossible task of reconciling the opinions of those who hold that the history of Australia has been essentially a triumphal march to the east, with those others who see it as a dogged retreat to the west. It is patent that divergences such as these cannot be coaxed into parallelism and we are perforce left with the task of examining seriatim the several interpretations of our continental evolution.

Although many geological papers deal in part or by implication with the development of Australia, three principal hypotheses have been formally propounded. These, in the order in which they appeared, may be called, for convenience, the hypotheses of Marginal Growth, of Continental Fracturing, and of Progressive Welding respectively. The first and third of these are clearly related and both may be regarded as hypotheses of constructive advance. The second, by contrast, is an hypothesis of destructive retreat.

The hypothesis of marginal growth was advanced by an early and powerful school whose influence is still strongly felt and who held that the Australian continent was originally only half its present size, extending no farther to the east than a line joining Darwin and Melbourne. From this small beginning the continent was supposed to have advanced step by step towards the east, the continental shelf of one period becoming the coastal strip of the next. In this way, lifting itself by its own boot-straps as it were, the little continent marched into the Pacific. Jensen (1911), although he does not claim to be the originator of the hypothesis, is the author who has stated it most explicitly and in greatest detail. Several geologists, including E. C. Andrews in particular, have pointed out that other aspects of our geological history were in keeping with this simple programme, and that the history of diastrophic events and of the major plutonic intrusions, together with the spatial distribution of ore-bodies, were all consistent with the one general plan. So that, in the end, Australian geologists had visions of an aggressive and completely organised army, horse, foot and artillery, advancing successfully upon the Pacific in a veritable "Drang nach Osten". The result of this advance was claimed to be the consolidation of the Australian continent, much as we know it now, and the (temporary) acquisition of a large mobile area to the east. Even as late as 1932, Sir Edgeworth David (p. 49) remarked in his "Explanatory Notes" that "as regards the evolution of the Australian continent, the point has frequently been stressed that after the disappearance of the Proterozoic Nullagine seas, deposition was mostly restricted

to what is now the eastern portion of the continent, and that there was a steady gain of land eastwards at the expense of the sea ”.

Although this attractive theory was based largely upon interpretations of events restricted to the Palæozoic era it came in time to be regarded as an epitome of our complete geological history. Indeed it developed ultimately into what was virtually a philosophical background for Australian geology. The Australian continent was seen as a stable unit, the result of a number of victorious conflicts, followed by final consolidation of the positions successively won. These ideas were seldom explicitly stated, but their implications may be detected intricately interwoven through many a writing on the history and growth of our continent. In particular they are clearly visible in the most recent statements of Andrews, who, however, as we shall see in the sequel, no longer agrees with the theory of marginal growth in its simple original form.

The second hypothesis, that of continental fracturing, was introduced not by an Australian but by the eminent American geologist, Schuchert (1916, p. 94), who challenged the commonly accepted thesis of marginal growth and launched another that was radically different. Schuchert's hypothesis was built upon the assumption of an originally great continental mass that became progressively smaller by loss to the Pacific. It replaced the very small pre-Cambrian continent of the earlier hypothesis by a very large one; the marginal seas of the Palæozoic by a central Mediterranean (the Tasman geosyncline); a migrating locus of deposition by a relatively fixed one; a continent growing at the expense of an ocean, by an ocean growing at the expense of a continent! Schuchert saw Australia not as a stable unit achieved by constructive effort, but as the shrunken remnant of a disintegrated continent.

Such a startling statement from one who was already recognised as a world authority on stratigraphy and palæogeography would, one might expect, have caused a sensation in geological circles in Australia. It did not, as far as I can gather, create even a ripple. The basal philosophy underlying the interpretation of the growth of a continent had been turned topsy-turvy—and apparently nobody cared. At least there was no immediate reaction expressed in the printed word.

The third hypothesis, that of progressive welding, is clearly a lineal descendant of the hypothesis of marginal growth to which it bears a strong family resemblance, and although they differ in important respects they are both imbued with the same spirit. The chief sponsor of progressive welding is Andrews, who has stated his case clearly and explicitly in two recent papers (1937, 1938). In his own words, “the nuclei of the existing continent appear to have been formed, step by step, far back in pre-Cambrian time, by a process of marginal growth, by the addition, or accretion, of mountain chains. These mountain systems are composed in the main of rocks which have been subjected to severe compression or folding. In the late pre-Cambrian, these blocks, once coextensive as surface features, appear to have been separated by the formation, within them, of structural depressions. A reasonably safe point for the start of our studies, however, appears to be the closing pre-Cambrian period.”

“Beginning then, at this stage, it may be shown that the stable block known today as Australia (with Tasmania) has resulted from the welding, or knitting, together of these ancient nuclei. This welding, fusion or stabilisation, took place, almost wholly, during the Palæozoic era.”

The relationship of this to the first hypothesis is clearly exhibited in these quotations and is also shown in passages such as this (p. 182): “great arcuate belts of Silurian, Devonian, Carboniferous and Permian rocks in this region [New England and eastern Queensland] were attached successively, as dry land, to the growing continent of Australia ”.

On the other hand the important differences which separate this variant from the original hypothesis and which show the belated influence of Schuchert's hypothesis are (1) the recognition that the pre-Cambrian basement extended at least as far as the limits of the present continent; (2) the acceptance of the Tasman geosyncline as a major geological structure; (3) the addition of the Palaeozoic borderland of Tasmantis. But these appear as admissions almost grudgingly conceded. Thus Andrews represents the Tasman geosyncline as an extraordinarily narrow, ribbon-like feature, confined within the present continental limits, while the borderland of Tasmantis as depicted by him appears quite inadequate for its important geological rôle. In these and other points the hypothesis of progressive welding exhibits the awkward misfits of unhappy compromise.

Although the three hypotheses differ in many minor details, they are most widely at variance in their opinions as to the former extension of the Australian continent into what is now the Pacific Ocean.

In searching for evidence bearing on this most controversial question, the critical region for investigation is obviously the easternmost strip of Australia as we now know it. Consideration of the structure and history of this area may well supply us with that link between the known and the unknown which we are endeavouring to find.

This critical region, we should note was, according to Schuchert, occupied by the western half of the major structural and geographical feature that he called the Tasman geosyncline, the eastern half lying beneath the Tasman Sea, from which it got its name. Schuchert showed the geosyncline as a persistent trough "which began to appear as a seaway in the Ordovician, had its greatest development in the Devonian" and "continued with some interruptions throughout the Carboniferous and Permian". It was completely enclosed at its northern end which, in the Permian, is shown as near Cape York, and had a large opening at its southern end between Tasmania and the southern end of New Zealand.

Much detailed information about the geology of this part of Australia that was not available when Schuchert published his paper is now at hand, and it is pertinent to enquire as to the bearing of this later knowledge on the question at issue. In particular our information concerning south-eastern Queensland is now far less incomplete as a result of Denmead's (1927) valuable investigations. We now know that the oldest rocks of this easternmost part of Australia are the Greenstones, which form the basal series of that large assemblage of sedimentary and volcanic rocks, metamorphosed to varying degrees, which we know collectively as the Brisbane Schists. The Greenstone Series is made up almost entirely of metamorphosed sub-basic and basic volcanic rocks which, though they display some variety, quite obviously all belong to the one suite. The base of the series is not visible, but Denmead now estimates their thickness from the lowest known horizon to the top of the series as 10,000 feet. The age of the Greenstones is unknown but David (1932, p. 36) suggested an age "between Proterozoic and Ordovician" and assigned them tentatively to the Newer Proterozoic.

Conformably above the Greenstones and merging into them by interbedding lie the basal members of the Bunya Series. The series consists essentially of grey and green mica phyllites (locally represented by quartz mica schists), with phosphatic cherts, slates and quartzites in the upper portion. The series as a whole presents remarkable uniformity over a great thickness, estimated by Denmead at 18,000 feet. Near the top of the series there has been found (and lost) one specimen diagnosed as a *Diplograptid*, on the strength of which the Bunya Series has been assigned to the Ordovician. The 28,000 feet of phyllites

and greenstone below this horizon may, as David indicates, well cover the Ordovician, Cambrian and part of the Proterozoic.

The phyllites of the Bunya Series pass conformably and without any sudden lithological break into the Neranleigh Series. This is composed essentially of greywackes (non-calcareous) and thin-bedded quartzites with a total thickness of 15,000 feet. In the lowest part of the series one sees an alternation of sediments of the Bunya and Neranleigh types, but once the new sedimentary type (greywacke) is well established it persists with remarkable uniformity, showing a purity of facies comparable with that of the Bunya Series.

Both the Bunya and Neranleigh Series are essentially siliceous and the Fernvale Series which follows is extraordinarily so, being made up for the most part of grey and green banded cherts and red radiolarian jaspers. It is perhaps not so strikingly uniform as the two preceding series and differs from them in the more pronounced development of interbedded andesites. The top of the series is unknown, but Denmead estimates the visible thickness at approximately 10,000 feet. The age of the series cannot be directly determined, but latest estimates suggest that it is pre-Devonian.

At some time subsequent to the deposition of the Fernvale Series, the Brisbane Schists were folded into a large but simple anticlinal structure with a moderate dip to the east and an almost vertical dip to the west. Denmead, who first described this important feature, modestly referred to it as the "Indooroopilly Anticline", but David was so seized with its importance that he promoted it to the "Brisbane Geanticline" and showed it as one of the few text figures in his Explanatory Notes, describing it as a "vast denuded geanticline perhaps originally 30,000 feet high".

The evidence presented by the several series of the Brisbane schists is cumulative, mutually-confirmatory and free of ambiguity. It points to the presence of a geological structure, the many features of which are so consistently those to be expected in a geosyncline that it may be regarded not merely as typical but as exemplary of its kind.

In particular the Greenstones exhibit just those chemical, mineralogical and petrological features that we might expect as the result of vulcanicity related to the establishment or previous existence of a geosyncline. The Bunya Series is composed of a great thickness of sediments all of which indicate deposition in deep quiet waters possibly far from land. The greywackes of the Neranleigh Series are also characteristic of geosynclinal sediments, although suggestive of deposition nearer one of the geosynclinal margins. The radiolarian jaspers and banded cherts of the Fernvale Series are again characteristic geosynclinal deposits and indicate a reversion of conditions to deeper and clearer water further from land, while the accompanying interbedded andesites are the very volcanics to be expected under these conditions.

Throughout the whole range of the Brisbane Schists totalling well over 50,000 feet, there is a remarkable absence of normal conglomerates, sandstones and limestones. Except for radiolaria, one graptolite and certain indefinite carbonaceous markings are the only signs of life. These negative criteria added to the positive criteria based on the uniformity and persistence through great thicknesses of the appropriate lithological types fully satisfy the conditions for geosynclinal sedimentation (as opposed to that of shelf seas) as recently set out by O. T. Jones (1938) in his presidential address to the Geological Society of London, "On the Evolution of a Geosyncline".

The evidence and conclusions outlined above have all been collected from one small area, deliberately chosen, first for its critical geographical position and second because it has been studied in considerable detail.

But the Brisbane Schists are by no means confined to this small area. The Greenstones, it is true, seem to be somewhat localised, but I have examined rocks

typical of the Bunya phyllites from Nambucca Heads (N.S.W.) in the south to Emu Park (Queensland) in the north, a distance of over 600 miles. The Neranleigh greywackes also have their counterparts in north-eastern New South Wales, while Professor Richards and I have seen them typically developed on the Keppel Islands. The Fernvale jaspers have been confidently correlated with the Woolomin Series of New South Wales, and they too have been traced as far north as Rockhampton.

It may well be that these series are represented even farther to the south and north. Indeed my colleague, Captain F. W. Whitehouse, informs me that he has recognised the principal types of the Brisbane Schists from Narooma, on the southern coast of New South Wales, to the highlands of New Guinea. At the very least, there is ample evidence that closely similar lithological types were deposited in the same sequence over an established length of 700 miles.

With regard to the width of the area in which these geosynclinal deposits were laid down, there is little direct evidence. To the west the same bathyal types persist with no suggestion of change until they disappear beneath a cover of later rocks. To the east, the typical deep-water deposits vanish under the sea, but a clue as to a possibly restricted extension in this direction during the deposition of the Neranleigh Series is provided by the greywackes themselves, which are not so typical of the median portion of a geosyncline, and more particularly by certain gritty beds in the valley of the Nerang River, which contain rounded boulders to two feet in diameter and which as Denmead (1927, p. 84) points out are of a rock unknown in southern Queensland. In general it would seem likely that the original width of the geosyncline must have been considerably greater than the width of the deep-water sediments that now represent it, and in particular that (except possibly in Neranleigh times) the eastern margin was well out under the Tasman Sea.

The igneous activity associated with the Brisbane Schists was restricted to that characteristic of geosynclinal conditions, namely contemporaneous flows and tuffs of a sub-basic and basic character. These, after providing an impressive prelude, as the Greenstone Series, form a recurrent theme, albeit with some minor variations, that is still dominant at the top of the Fernvale Series.

There was a notable absence of folding movements during the deposition of the Brisbane Schists. The several series are all conformable and grade one into another and the regional metamorphism of similar lithological types becomes gradually less intense with each successive series. The simple but enormous structure of the Brisbane geanticline, the formation of which closed the history of the Brisbane Schists, has all the features to be expected of a median geanticline produced during the uplifting of bathyal deposits that had been accumulated in the middle of a trough.

On the evidence provided by the Brisbane Schists alone (and it must be remembered that this evidence was not available to Schuchert) one may deduce that a large geosyncline, at least 700 miles in length, extended to the north beyond Rockhampton and to the east well beyond the present coast line; further, that the geosyncline was already fully established at the beginning of the Palæozoic era. The essential simplicity of this major geographical feature during a large part of geological history as shown by persistence of facies, constancy of position and absence of overfolding and overthrusting, suggests further that, at least in this stage of its evolution, the Tasman geosyncline was sheltered to the east, not by a narrow mobile borderland, but by a broad stable buttress of almost continental dimensions; that the Brisbane Schists were laid down in a mediterranean sea in the heart of a great Australasian continent.

If we wish to continue our inquiry into the evolution of the Tasman geosyncline we must leave the Brisbane area and move, not to the east and

north as the hypothesis of marginal growth would suggest, but to the west and south. There at Silverwood Professor Richards and I (1924) have investigated a series of jaspers very similar to those of the Fernvale (and Woolomin) Series and presumably coeval with them, which is followed by the 6,000 feet of andesitic and spilitic volcanics which constitute the lower half of the Silverwood Series. Almost at the top of these very uniform volcanic rocks are the lenses of coralline reef-like material known as the Silverwood Limestone. This horizon has several points of interest. It is the first strongly developed calcareous type met with in the history of the geosyncline as developed in southern Queensland; it presents us with the first really satisfactory evidence of shallow water conditions; it is the first horizon the age of which (Couvinian) can be definitely determined. But the Silverwood Limestone did not herald a permanent change from the bathyal facies, for it was very shortly followed by banded radiolarian cherts and shales showing that conditions of deposition were again essentially similar to those of the Fernvale Series. The top of the Silverwood Series is unknown but there are at least 5,000 feet of banded shales becoming progressively less chertified as the series is ascended.

Since the hypothesis of progressive welding agrees with that of continental fracturing in admitting the existence of the Tasman Geosyncline from the Devonian to the end of the Palæozoic era, there is no need for the further review of the evidence bearing on the continued existence of that structure. Suffice it to say that the first definite change from sedimentation of the bathyal type (and the dominance of siliceous rock types), to typical neritic deposits (of dominantly calcareous type), appears within the Carboniferous strata of the Rockhampton Series. After that change there is no further reversion to deep-water sedimentation but, on the other hand, there is, following the development of Permian paralic deposits in many parts of eastern Australia, a transition to lacustrine and terrestrial conditions. Perhaps the outpourings of andesitic lavas and tuffs that preceded the deposition of the lowest of the Mesozoic fresh-water deposits in southern Queensland (the Andesitic Boulder Beds at the base of the Esk Series) mark the final manifestation of the influence so long exerted in eastern Australia by the Tasman Geosyncline.

A suggested interpretation of the development of the Tasman Geosyncline in southern Queensland is shown in the accompanying table.

When we assemble all the available data, including that of the Brisbane Schists, we have, I suggest, adequate evidence of the existence of one of the major geographical features of the world, a feature comparable in size with the Mediterranean Sea which now separates the continents of Europe and Africa and a feature which remained virtually constant in position throughout the whole of the Palæozoic era. In its size and persistence, although not in the minor details of its development, it is comparable with the great Appalachian Geosyncline of North America.

The rival hypotheses of Schuchert and Andrews, although they agree as to the existence of the Tasman Geosyncline in Upper Palæozoic times, do not, however, agree as to the nature and extent of the continental mass beyond the geosyncline. Schuchert pictures it as "the eastern half of the Australasian continent, a land about 1,800 miles east and west and 2,200 miles north and south". Andrews, although he points out that the limits are unknown, pictures it as of far smaller dimensions.

Sussmilch and David (1920, p. 277) evidently regarded it as of considerable size and referred to it as "a separate land area [in the Carboniferous] which existed to the east of the Australian continent at least as far back as the beginning of the Devonian period and probably as far back as the beginning of the Palæozoic era". They stated further that this land, which they suggested should be

THE TASMAN GEOSYNCLINE AS DEVELOPED IN SOUTHERN (AND CENTRAL)* QUEENSLAND.

Eras.	Series.	NATURE OF SEDIMENTATION.			Epochs of Andeastic Activity.	History of Geosyncline.
		Geosynclinal.	Littoral.	Paralic.	Lacustrine.	
Mesozoic.	Esk, Upper.					Lacustrine Conditions.
	Esk, Lower.				Conglomerates, sandstones and shales.	
	Fault Blocks, Upper.				Andesitic boulder beds.	Transition.
	Fault Blocks, Lower.			Fresh-water shales interbedded with marine sandstones.		
	*Rockhampton, Upper.		Grits, sandstones.			Neritic Phase.
Palaeozoic.			Oolitic limestone, grits and sandstones.		Localised and intermittent (as at Gympie).	
	*Rockhampton, Lower.	Shales and cherts.				Transition.
	Silverwood, Upper.	Banded radiolarian cherts and shales.				
	Silverwood, Lower.	Small coral reefs, Andesites and spilites.			Continuous and on considerable scale.	Bathyal Phase.
	Ferrvale.	Red radiolarian jaspers, green handed cherts and andesites			Intermittent.	
Proterozoic.	Neranleigh.	Greywackes with quartzites			Occasional and local.	Initiation?
	Bunya.	Grey and green phyllites and slates, with quartzites				
	Greenstone.	Andesites, spilites, porphyrites and basalts.			Continuous and prolonged on grand scale. Volcanic Prologue.	Initiation?
	? ? ? ?					

* With the exception of the Rockhampton Series, all these formations are well represented within 100 miles of Brisbane.

known as "Tasmantis", "became permanently united to the mainland towards the close of the Permo-Carboniferous Period".

When we leave the Palæozoic history of Australia and enter the Mesozoic, the three hypotheses which deal formally with the evolution of the continent exhibit interesting developments. Andrews' hypothesis of progressive welding realigns itself with the original hypothesis of marginal growth, from which it had diverged, in affirming that the stabilisation of the small Australian continent was virtually complete by the end of the Palæozoic era. As a necessary corollary of this conclusion, the Mesozoic extension to the east, although admitted as such, was not recognised as constituting a positive step in the evolution of Australia. Rather it was considered spatially as no more than an excrescence of the true continent, and temporally as but a postscript to the story proper.

This attitude of depreciation is in strong contrast with that adopted by Schuchert, for whom the events of the Mesozoic were of the first importance as providing the basis for his thesis that the progressive disintegration of the eastern half of the great Australian continent occurred principally during that era.

Schuchert suggested that this supposed continental fracturing actually began before the close of the Palæozoic era. He advanced no specific reasons based on local evidence for this opinion, but apparently selected this time of widespread diastrophism in other parts of the world as an appropriate date for the initiation of the destructive forces in Australasia. But there is much local evidence to suggest that the Hercynian orogenies were not nearly so pronounced in Australia as elsewhere. Further, although the disappearance of the great Tasman geosyncline in late Palæozoic times marked a geographical and geological transformation of the first importance, it may be explained, without recourse to violent orogeny, as due to simple filling accompanied by gentle, if intermittent, uplift.

If this explanation be accepted it is unnecessary to assume any marked mobility in the complementary borderland at this time, still less the severe fragmentation that Schuchert shows in his late Palæozoic maps.

In conformity with his main thesis, Schuchert's Mesozoic maps depict the eastern half of Australasia as an archipelago, changing in the shape and distribution of its constituent parts from period to period. But, strangely enough they show a minimum of change between the Cretaceous and the Eocene, when the effects of the widespread Laramide revolution might have been expected to have brought about important geographical modifications, especially as this orogeny is well represented in Queensland, New Caledonia and New Zealand.

At this stage attention should be drawn to the work of Walkom (1918) who, having specialised in the study of the Australian Mesozoic deposits, published an instructive series of maps which were radically different from those of Schuchert in that they showed the eastern half of Australasia, not as an ever-changing archipelago, but as a great continuous mass that persisted throughout the Mesozoic with no more marked geographical modifications than those exhibited by the other continents during that era. Such changes as he shows, and more especially the impressive redistribution of land and water in the Lower Cretaceous, may well be regarded as no more than local examples of the widespread transgressions which flooded all the continents, including Australia proper, at that time and which thereby provided maximum geographical changes accompanied by only a minimum of structural deformation.

Benson (1923, 1924) gave strong support to Walkom's main conclusions as to the Mesozoic extension of the continent and introduced modifications and elaborations of his own based on numerous geological details collected from the scattered literature. These he marshalled with meticulous care in his two important papers dealing respectively with the palæogeography of Australasia and the nature of its structural margin.

A most important item in the several attempted reconstructions of the Australasian region in Mesozoic times concerns the relationship of New Zealand to the main Australian mass. Schuchert, in accordance with his scheme of early fragmentation showed the two regions as definitely divorced early in the Triassic. Marshall (1933), in an address which reads almost like a declaration of independence, emphasised the many differences between New Zealand and Australia and expressed the opinion that the former has been a separate and distinct unit at least since the Middle Mesozoic. Walkom, on the other hand, shows New Zealand as part of the one continuous land area as late as the Lower Cretaceous, while Benson's map pictures the two regions as still securely linked in Upper Cretaceous times.

The possibility of such diverse interpretations on this matter as on other aspects of our Mesozoic palaeogeography is, of course, due to the fragmentary nature of the evidence on which, in common, they are based, and which consists of the incomplete geological records of a few widely scattered localities.

The only points of general agreement in the several interpretations of the Mesozoic era appear to be that (1) an eastern extension of the Australian continent (either in the shape of a continuous mass or a detached archipelago) reached far out into the Pacific, and (2) at least by the end of the era "the various portions of Australasia ceased to have any striking unity of geological history" (Benson, 1923, p. 53).

At the beginning of the Tertiary era there were then, in the Australasian region, a number of independent geographical units which, by that time, appear to have achieved some geological independence as well. But, if the seismological evidence is to be accepted, these units are all nevertheless part of one continuous sheet of sial extending eastward from Australia and clearly circumscribed by a well defined and active seismic zone.

It is difficult, if not impossible, to reconcile this unity and disunity as both due to the same evolutionary process. In particular it is difficult to explain them both in terms of circum-Pacific relationships. For these latter, although they exhibit some variety of expression, are always and everywhere consistent among themselves and all are variations of the same compelling process. It would seem that the origin of the Pacific, however it may have been brought about, produced, as an immediate and direct consequence, the setting up of an essentially simple structural relationship between the ocean basin and the surrounding continental masses. This expressed itself as movements of compression concentrated in a circum-Pacific mobile belt or hinge area in which the stresses as between ocean and continent were accommodated. This compression manifested itself most clearly as overfolding and overthrusting of the circum-Pacific continental rim towards the Pacific basin, but complementary underthrusting outward from the basin may have been equally pronounced although more difficult to prove.

Such an essentially simple structural relationship would, I suggest, tend to perpetuate the pattern originally imposed—not to destroy it. There might and probably would result changes in the area of the Pacific from time to time, but the primal pattern would persist with little modification. But in the south-western sector of the Pacific the pattern is now only weakly displayed. Indeed the geographical evidence of its very existence is incomplete and ambiguous. Fortunately, the seismic evidence is clear and direct, but the continuity of sial from Australia to the Marshall Line and the well-defined seismic zone are almost the only Australasian witnesses to the unity and persistence of the Pacific structure.

Between Australasia and Antarctica even the seismic evidence is incomplete and the pattern disappears, and in place of the Pacific rim there is only a region of subsidence.

It is difficult to see how this foundering in the south-west quadrant can be reconciled with the inherited circum-Pacific forces in which tension is only an occasional and incidental factor. And why should forces which elsewhere tend to perpetuate a well established plan seek, in Australasia, to destroy it?

Is it not more probable that this movement had a completely different and independent origin? May it not have been due to the imposition of an extraneous force on an area previously dominated by the circum-Pacific control, with the result that the effects of the latter were almost neutralised in Australasia and quite negatived near Antarctica?

Only a force of world-wide dimensions would, I submit, be capable of disturbing the balance of the great Pacific structure, and of interfering with its directive mechanism. Schuchert, we have seen, invoked just such a world tendency to explain the fragmentation of the continents and especially of Australasia, but he believed it to have been initiated even before the Mesozoic, not as is here suggested, at the close of that era.

If we are right in thus regarding the foundering of Australasia as independent of and in actual conflict with the circum-Pacific control, then the expansion of that ocean in the Tertiary era no longer appears as a successful advance, for it has been made only at the expense of its own unity. Geographical extension in such circumstances is as much an indication of structural failure as is geological collapse. Consequently phrases such as "the Pacific has grown at the expense of Australia" are misleading, and untrue except in the strictest geographical sense. Emphasis should, I think, be laid on the concept of Australia and the Pacific as partners equally involved in the failure of an apparently well-established mechanism which previously had preserved their mutual relationships.

CONCLUSION.

We have now covered the ground we set out to traverse and, although the survey has necessarily been a hurried one, I submit that the evidence examined, although by no means conclusive, is consistent with the following propositions:

- (1) That the basin of the Pacific Ocean is the greatest and most important of terrestrial structures.
- (2) That as a structure it is homogeneous, permanent and unique.
- (3) That the structural boundary of the Pacific basin, in the south-western quadrant, is represented by the Marshall Line.
- (4) That a great Australasian continent existed immediately to the west of this Line from as early as pre-Cambrian times and persisted throughout the Palæozoic and Mesozoic eras.
- (5) That forces of extra-Pacific origin brought about the dismemberment of the Australasian continent in early Tertiary times.
- (6) That nevertheless the structural limit of the original Australasian mass is still clearly indicated by a well-defined seismic zone.

It will be seen that the adoption of this interpretation of the relationship of the Australian continent to the Pacific Ocean necessarily involves the denial alike of hypotheses of Palæozoic expansion and of Mesozoic decline, and definitely precludes the acceptance of the present Australian continent as a complete geological unit.

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NOTES ON THE NOMENCLATURE AND TAXONOMY OF CERTAIN SPECIES OF *MELALEUCA*.

By EDWIN CHEEL.

Manuscript received, June 19, 1944. Read, July 5, 1944.

THE STATUS OF *MELALEUCA FASCICULIFLORA* Benth.

In working out a plant from South Australia, which is apparently *Melaleuca fasciculiflora* Benth. (1866), certain difficulties arose in connection with the spelling of specific names and citation of papers published by Turczaninow, on the Myrtaceae collected by Drummond in Australia. As no copy of Turczaninow's paper was available in any of our libraries I wrote to Sir Arthur Hill, Director of the Royal Botanic Gardens, Kew, England, who very kindly submitted my queries to Mr. T. A. Sprague for report, with the result that I am now able to clear up some of the discrepancies between the citations given in Mueller's "Fragmenta" and those given in "Index Kewensis". The following notes deal with certain species of *Melaleuca*, of which there is an abundant collection of herbarium material in the National Herbarium of Sydney, collected by various collectors in different parts of South and Western Australia. Examination of the material of *M. fasciculiflora* Benth. leads to the conclusion that Benth. included three distinct species under that name, viz. *M. bracteosa* Turcz., *M. brevifolia* Turcz., and *M. decora* (Salisbury) Britten, q.v.

Melaleuca bracteosa Turcz. (1822), vide "Index Kewensis".

In Mueller's "Fragmenta", VIII (1872-1874), 184, the spelling is given as "*bracteata*", but according to Mr. Sprague, who has kindly looked up the original work of Turczaninow at my request, the spelling and citation given in "Index Kewensis" are correct. This is particularly important since there is a *M. bracteata* F.v.M. in "Fragmenta", I (1858-1859), 15, which is united with *M. genistifolia* Sm. by Benth. (1866), but since regarded as a valid species by Baker and Smith (1910), with which I am entirely in accord. Turczaninow's paper, "Myrtaceae Xerocarpicae, etc.", was originally published in *Bull. Phys. Math. Acad. Sc. St. Petersburg*, X, Col. 321-346 (1852), as stated in the Royal Society's *Catalogue of Scientific Papers*, Vol. VI, 66, No. 17. There are two columns per page, and the columns, not the pages, are numbered. Turczaninow's paper was reprinted in *Melanges Biologiques Bull. Acad. Petersb.*, I, 394-428, and it was this reprint that was cited by Mueller in his "Fragmenta", VIII, 182 (1872-1874), hence the discrepancy in the pagination. Alike in the Bulletin and the Melanges, the name of the species appeared as *Melaleuca bracteosa*, not *bracteata* as cited by Mueller.

Melaleuca brevifolia Turcz.

Syn. *M. fasciculiflora* Benth. in part.

Leaves alternate, crowded, 4-6 mm. long, distinctly petiolate (the petiole although small is more clearly defined than in Drummond's No. 159, which Benth. included with *M. fasciculiflora*—which is *M. bracteosa* Turczaninow), somewhat terete in general appearance but slightly flattened on the upper surface, sub-acute at the apex, or scarcely obtuse. Flowers sessile in lateral
G—July 5, 1944.

head-like clusters, frequently coalescing so as to appear to be in lateral spikes. Petals very deciduous, jagged along the margin. Stamens in bundles, the claw slightly shorter than the petals. Capsules 3–5 mm. diam., the rim comparatively thick, valves somewhat sunken. Drummond's No. 164 quoted by Benthham under *M. fasciculiflora* belongs to this species, as also the Gordon River specimen collected by Maxwell.

This species is quite distinct from *M. brevifolia* of Mueller, which is quoted as a synonym of *M. microphylla* by Benthham.

Melaleuca decora (Salisb.) Britten (1901).

Syn. *Metrosideros decora* Salisb. *Melaleuca genistifolia* Sm.

The original specimens described by Salisbury (1796) were collected by David Burton in the Port Jackson district. It was placed in the genus *Metrosideros* but afterwards transferred to *Melaleuca* by Smith (1797), who evidently had not seen Salisbury's specimens, hence the specific name "*decora*", which has a prior claim, was not taken up. According to Benthham (1866), who records it under the name *M. genistifolia*, it has a very wide distribution in Australia, but, as he included *M. lanceolata* Otto (1822) and *M. bracteata* Mueller (1858–59) as synonyms, which are now recognised as distinct species, the localities mentioned by Benthham for *M. genistifolia* (= *decora*) and copied by various botanists may have to be considerably reduced. Specimens in the National Herbarium of Sydney are represented from numerous localities along the coast from Sydney to Nowra in the south, and as far north as Newcastle, extending to Bullahdelah, Stroud, in New South Wales, and Jimboomba and Sunnybank in Queensland. (Burton states that the plant was commonly known as "White Tea Tree". In Queensland it is called "Ironwood" or "Ridge Myrtle".

Melaleuca lanceolata Otto (1822).

Syn. *M. genistifolia* Baker and Smith (1910) non Smith (1797); *M. parviflora* Moore and Betcher (1893); *M. parviflora* var. *latifolia* Maiden and Betcher (1916).

This is a tall shrub or small tree from twenty to thirty feet tall with white papery bark and small flat acute lance-shaped leaves, usually about one-half to three-quarters of an inch long, and not revolute or tapering as in *M. decora* and *M. bracteata*. It has been confused with *M. parviflora* Lindley¹ (1839) and *M. decora*. It is quite common in the Gosford district, extending to the Crawford River near Bullahdelah and Wallace Island.

Melaleuca bracteata F.v.M. (1858–59).

The original specimens described by Mueller (1858–59) were collected at Moreton Bay in Queensland, and regarded as an intermediate species between *M. styphelioides* and *M. curvifolia*. Benthham linked it as a synonym under *M. decora* (syn. *M. genistifolia*), but as shown by Baker and Smith (1910), it is quite distinct. It is a small tree from twenty to forty feet tall, with a rough brown bark and somewhat umbrageous habit, usually found hugging the sides of creeks and rivers, very plentiful between the Gwydir and McIntyre Rivers in the Boggabri and Narrabri districts, extending to Bingarra and Warialda and thence to Lismore and as far north as Rockhampton in Queensland.

The specimens included under *M. genistifolia* by W. V. Fitzgerald (1918) and by Ewart and Davies (1917) from the Kimberleys in north-west Australia and Northern Territory respectively, as well as those from the Torrens River,

¹ See Cheel (1926), where *M. parviflora* of Lindley is treated as a glabrous form of *M. pubescens*.

Mueller (1856), and Ord River, Mueller (1880), are very probably sufficiently distinctive to be regarded as a variety or new species.

MELALEUCA NERVOSA (LINDL.) CHEEL N. COMB.

Syn. *Callistemon nervosus* Lindl. (1848).

This species was described by Lindley from specimens collected at Mitchell's Camp of 16th July, 1846, which is quite close to Mantua Downs on the Claude and Nogoia Rivers, south of Springsure, north Queensland. At p. 235 of Mitchell's work the following remarks are published: ". . . and we found a magnificent new crimson *Callistemon*, with its young flowers and leaves wrapped in wool". In a footnote of the same work a description in Latin by Lindley is published as follows: "*ramis pallidis foliis ovato-lanceolatis, quinque-nerviis mucronatis junioribus tomentosis, rachi calycibusque lanatis*". It will be noted that no mention is made of the cohering of the filaments by Lindley, hence there has been much confusion concerning this species as to whether it should be placed in *Callistemon* or *Melaleuca*.

Callistemon nervosus Lindley is included by Bentham as a synonym under *M. Leucadendron* var. ? *parvifolia* (rock, Balmy Creek, in the interior of Queensland, Mitchell).

In a previous paper (Cheel, 1917, p. 298) I included *M. Crosslandiana* W.V.Fitzg. as a form under *M. leucadendron* var. *coriacea*, and stated that it differed only "in the flowers being crimson", whereas in var. *coriacea* they were greenish-yellow. Since the publication of the above, a communication received from Mr. Fitzgerald contained the following remarks: "I do not agree with Mr. Cheel in assigning *M. Crosslandiana* to *M. leucadendron*. Besides the crimson filaments mentioned by him, there are other details, including the rough, fibrous, persistent grey bark and hard reddish-brown timber of the former. It is certainly not a "Paper-bark". In view of this further information, together with a fuller description published by Fitzgerald (1918)—which I had not seen previously, I am now of the opinion that *M. Crosslandiana* W. V. Fitzgerald should be included as a synonym under *M. nervosa* (Lindl.) Cheel.

On the subject of the generic distinctions between the two genera *Callistemon* and *Melaleuca* the remarks of Mueller (1863-64), which are in Latin, and may be translated as follows, are of interest: "The genus *Callistemon* is in my opinion, entirely artificial, not safely distinguished from *Melaleuca* by a single character and better united with it. Even the species which is the type of the genus *Melaleuca* i.e. *M. Leucadendron*, which abounds from the vicinity of Port Jackson through East and North Australia has a doubtful position between the *Melaleucas* with fascicled stamens and the true *Callistemon* as originally observed by Brown. Thus *Callistemon nervosus* Lindley belongs to *Melaleuca Leucadendron* var. *minor*. This species varies extremely in habit; in moist valleys and on river banks, occasionally subject to inundation, the tall arborescent form is found; in arid, stony and sandy tracts the low tree or shrubby form is found. The filaments appear sometimes whitish-yellow and sometimes citron-yellow, the height is also very variable; the staminal bundles adhere occasionally at the base in a ring as happens also in *Callistemon lanceolatus*, and often they are all free; the filaments of the staminal bundles are sometimes only very slightly united and sometimes considerably. The bark of several species is paper-like and flakey."

Notwithstanding the remarks of Mueller, Bentham (1866, p. 124) regarded the genus *Melaleuca* as a "well-defined group readily distinguished from *Callistemon*, by the 5-adelphous stamens . . . The only exceptions are one or two species in which the claws of the staminal bundles are so short as to connect the genus with *Callistemon* of which one species *C. speciosus* has the stamens almost

or quite 5-adelphous, but single transitionary species appear scarcely to justify the union of very large groups otherwise well characterised." The species *C. speciosus* referred to by Bentham was originally described by R. Brown (1812) as *Melaleuca paludosa* (and is retained in the genus *Callistemon*, as the venation of the leaves is characteristic of all the species of the latter). The species *Callistemon lanceolatus* mentioned by Mueller above was also noted by Bentham (1866) as having the "stamens united at the base"; a compound description was drawn up for both species by Bentham. Britten (1901, p. 37) published a Latin description copied from Solander's Mss. together with a drawing (Fig. 109) of a plant collected by Banks and Solander in 1770, on the Endeavour River, which he erroneously classified as *Callistemon rigidus*. This is *Metrosideros viminalis* Gaertner, I, 171 (1788), tab. 34, Fig. 4, which includes *C. lanceolatus* Mueller and Bentham in part, mentioned as having been collected by Fitzalan on the Pine River in Queensland.²

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² See Cheel (1917) in Maiden's *F. Fl.*, VII, 15, for further particulars concerning these two species under *C. viminalis* (Sol.) Cheel.

THE CHEMISTRY OF BIVALENT AND TRIVALENT RHODIUM.

PART VII. COMPLEXES WITH DIETHYL SULPHIDE.

By F. P. DWYER, M.Sc.,
and R. S. NYHOLM, M.Sc.

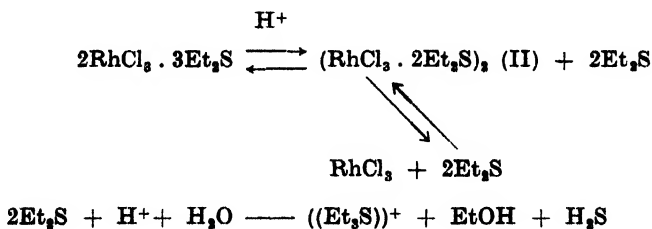
Manuscript received, June 7, 1944. Read, July 5, 1944.

Coordination compounds of the dialkyl sulphides with the elements of Group 8 have been extensively studied in the cases of platinum, palladium and iridium, the former two elements of which yield well defined compounds of the general type $\text{MX}_2 \cdot 2\text{R}_2\text{S}$ (Jensen, 1935; Angell, Drew and Wardlaw, 1930; Mann and Purdie, 1935), while trivalent iridium compounds $\text{IrX}_3 \cdot 3\text{R}_2\text{S}$ have been described by Ray and Adikari (1934).

In the present investigation, the compounds of rhodic halides with diethyl sulphide have been studied, and attempts have been made to reduce these compounds in accordance with the usual procedure, to the corresponding bivalent compounds. In all cases the reduction has failed, owing, it is suggested, to the weakness of the bond between sulphur and rhodium in the trivalent compounds and the probability that in the bivalent compounds this bond would be even weaker. This latter suggestion is supported by the fact that diethyl sulphide fails to coordinate with the more basic members of Group 8—iron, cobalt and nickel—and in the cobalt sub-group, reacts only slowly and incompletely with trivalent iridium which is markedly more acidic than trivalent cobalt or rhodium. Bivalent rhodium has been shown to be distinctly basic—the oxide showing no amphoteric properties (Dwyer and Nyholm, 1941).

The rhodic compounds possessed the general formula $\text{RhX}_3 \cdot 3(\text{Et}_2\text{S})$ (I) and were usually prepared by heating the rhodic halide with an excess of the coordinating group in aqueous alcoholic solution. Coordination took place slowly, and incompletely, and at room temperature was incomplete even after a day. The resulting compounds had a strong odour of diethyl sulphide both in the solid state and in solution, while the molecular weight determinations gave evidence of dissociation. The solubility in organic solvents was very high, and alcoholic silver nitrate precipitated the silver halide only on boiling.

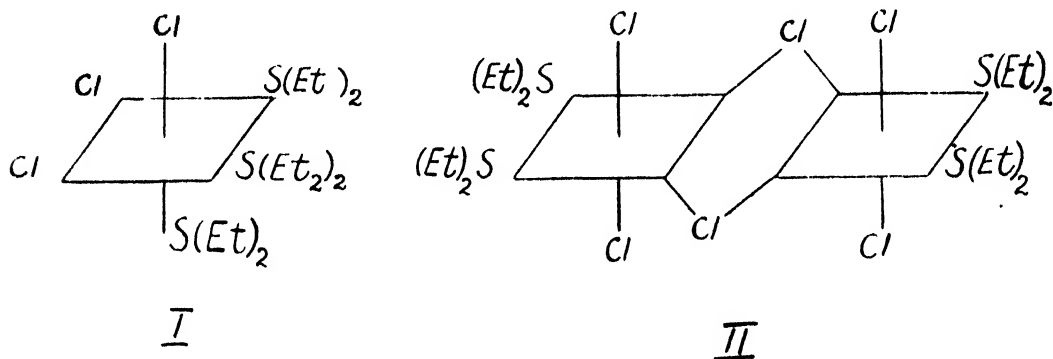
In hot acid alcoholic solution dissociation occurred, followed by destruction of the diethyl sulphide until ultimately the pure rhodic halide was left behind, according to the following scheme:



Although pure specimens of compound II were not isolated, impure specimens were obtained from time to time.

Further evidence of the weakness of the bond between the rhodium and the sulphur in these compounds was found in the iodide complexes. Diethyl sulphide failed to react with pure precipitated rhodic iodide, while by the addition of potassium iodide to the chloride complex, nearly 90% of the rhodium was precipitated as rhodic iodide. Yields of the required complex were obtained by this latter reaction only in the presence of excess of diethyl sulphide. Finally, it was noted that diethyl sulphide failed to react at all with potassium rhodium thiocyanate, in which the metal is present as the stable red $(\text{Rh}(\text{CNS})_6)^{\text{III}}$ ion.

Reduction experiments on the rhodic complexes either formed *in situ* as in the cases of the arsine or pyridine complexes (Dwyer and Nyholm, 1942, 43), or on pure isolated specimens, were fruitless. The usual reducing agent, hypophosphorus acid, in halogen acid solution failed owing to destruction of the diethyl sulphide by the acid, and in the absence of the acid by the preferential formation of a complex hypophosphite, noted previously. Sodium formate and formaldehyde both slowly reduced the complex, but much more rapidly reduced the dissociated rhodium halide to the metal. Sodium sulphite gave an insoluble basic rhodic sulphite, while hydroxylamine failed to react. Diethyl sulphide itself, which is a mild reducing agent in acid solution, yielded black precipitates which were slowly soluble in concentrated hydrochloric acid and were apparently rhodous sulphide. Finally, it was noted that ethyl alcohol in hot neutral or faintly acid solution, while it failed to reduce the complex, reduced the dissociated rhodic halide to the dark red rhodous state, and then to the metal.



EXPERIMENTAL.

Tris-diethylsulphide trichlororhodium. Rhodium trichloride solution, 30 mls., containing 0.285 g. of rhodium was neutralised with caustic soda, and then made just acid with hydrochloric acid. Diethyl sulphide, 0.75 g. with alcohol 15 mls., and water 10 mls., was added and the solution boiled for one to two minutes. After cooling the mixture was precipitated with water, and the oily precipitate coagulated with petroleum ether. The yellow rods and plates melted at 126°C ., and were easily soluble in organic solvents, even hot petroleum ether, from which it crystallised on cooling.

Found: Rh=21.5%; Cl=22.3%. Calculated for $\text{RhCl}_3 \cdot 3(\text{C}_2\text{H}_5)_2\text{S}$: Rh=21.46%; Cl=22.2%.

Tris-diethylsulphide tribromorhodium. A faintly acid solution of rhodium tribromide, 90 mls., containing 0.855 g. of rhodium was treated with diethyl sulphide 2.5 g. and alcohol, 35 mls. The mixture was heated to boiling and maintained at that temperature for a minute. After cooling, the mixture was precipitated with water, and then recrystallised from aqueous alcohol twice. The substance crystallised in brilliant red leaflets and truncated rods, m.p. 107°C . An alcoholic solution of the substance when treated with alcoholic silver nitrate, precipitated the silver halide only on boiling.

Found : Rh=16.6% ; Br=39.3% ; mol. wt. (cryoscopic in benzene), 579. Calculated for $\text{RhBr}_3 \cdot 3(\text{C}_2\text{H}_5)_2\text{S}$: Rh=16.79% ; Br=39.15% ; mol. wt.=612.

The compound of type (II) Tetrabromotetrakis-diethylsulphide μ dibromo-dirhodium was not obtained pure in any experiment, but during the preparation of the tris compound above, in acid solution compounds were obtained which gave on analysis high results for both rhodium and bromine. After treatment with alcoholic diethyl sulphide or even recrystallisation the percentages of these constituents fell to those required for the tris compound. No pure compound could be isolated. A typical analysis was Br=43.1% ; Rh=18.8%.

Calculated for $(\text{RhBr}_3 \cdot 2(\text{C}_2\text{H}_5)_2\text{S})_2$: Br=45.8% ; Rh=19.66%.

These compounds were completely soluble in cold benzene, and contained no adsorbed rhodium or halogen.

Tris-diethylsulphide-triiodorhodium. Rhodium trichloride, 15 mls., containing 0.16 g. of rhodium was carefully neutralised with caustic soda, and treated with diethyl sulphide, 0.6 g., and alcohol, 20 mls. The mixture was heated to 80° C. to form the chloride complex, and a concentrated solution of potassium iodide, 3 g., in water added. The solution was maintained at 80° C. for three minutes, when a dark reddish black substance was precipitated. The mixture was cooled, treated with water and petroleum ether, and filtered. The black precipitate was dissolved in alcohol containing a small amount of diethyl sulphide, filtered from the insoluble rhodic iodide, and the dark red solution precipitated with water in the presence of petroleum ether. The reddish black monoclinic rods melted at 98° C., and dissolved readily in organic solvents to dark red solutions.

Found : Rh=13.7% ; I=50.8%. Calculated for $\text{RhI}_3 \cdot 3(\text{C}_2\text{H}_5)_2\text{S}$: Rh=13.65% ; I=50.39%.

SUMMARY.

The preparation of coordination compounds between rhodic halides and diethyl sulphide is described. Owing to the weakness of the link between bivalent rhodium and sulphur, attempts to prepare the rhodous complexes were unsuccessful.

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VOLUME LXXVIII

PART III

THE LIGHT ABSORPTION AND MAGNETIC PROPERTIES OF NICKEL COMPLEXES.

By H. A. MCKENZIE, D. P. MELLOR, J. E. MILLS AND L. N. SHORT.

Manuscript received, July 12, 1944. Read, August 2, 1944.

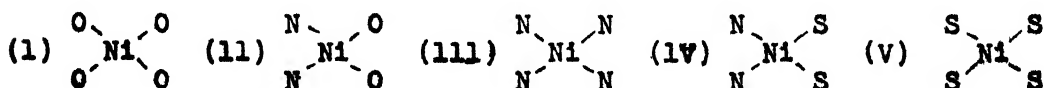
INTRODUCTION.

It has long been known that the colour of internal complexes of nickel such as bis-dimethylglyoxime nickel, is strikingly different from that of simple nickel salts and for a time there appeared to be a simple correlation between the colour of nickel compounds and their magnetic behaviour. Many paramagnetic nickel complexes are some shade of green or blue, while diamagnetic complexes have, as a rule, colours ranging from bright red through reddish brown to various shades of yellow. In the course of a survey of the magnetic properties of nickel compounds carried out in this laboratory it has become apparent that little reliance can be placed on the above correlation (Mellor and Craig, 1940). It has been found, for example, that vermilion bis-1-hydroxy-acridine nickel and deep wine red bis-thiolquinoline nickel are both paramagnetic, with moments of 3.2 Bohr magnetons in each case; that green formylcamphor-ethylenediamine nickel and green bis-salicylaldoxime nickel are diamagnetic.

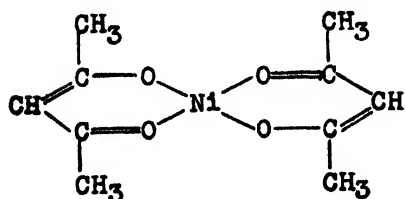
It is clear that colour, concerned as it is with absorption in the visible spectrum, is too superficial a basis for studying the correlation and that the absorption spectrum extending over the visible and ultra-violet region offers a more satisfactory basis for making comparisons. Furthermore, it is obvious that the light absorption of the organic addendum (or chelate group) in the compounds studied, must play a part in determining colour and that if we are to discover what influence the nature of the binding and the magnetic condition of the nickel atom has on its absorption of light, proper allowance must be made for absorption by the remainder of the molecule to which the nickel atom is bound.

In order to make such allowance, the procedure adopted in the present work has been to compare the absorption spectrum of the nickel complex with that of the chelate molecule (or molecules) from which it was derived, both compounds being studied in the same solvent wherever possible.

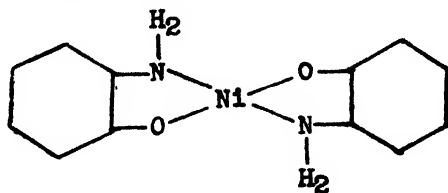
In the main, the substances which have been used as chelate groups, produce, under the dispersion used, relatively simple absorption spectra which enable the effect of introducing the nickel atom into the molecule (or molecules) to be more readily determined. It has been found convenient to classify the nickel compounds themselves according to the nature of the four atoms bound to the metal. Five classes have been considered:



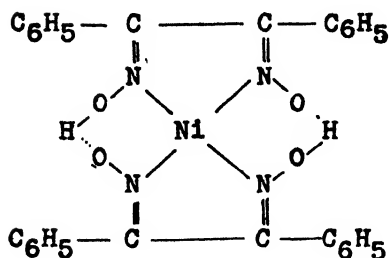
An example from each class is shown in I-V.



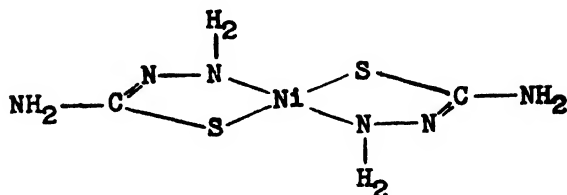
I.



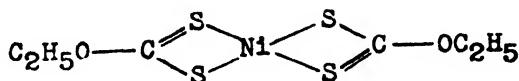
II.



III.



IV.



V.

EXPERIMENTAL.

The absorption curves were obtained by using a Hilger quartz spectrograph in conjunction with a rotating sector photometer and a condensed tungsten steel spark as light source. Spectra were photographed mainly on Kodak Orthochromatic plates. After the sector had been set at a predetermined value, match points were determined for two adjacent spectra, the intensity of one of which was controlled by the sector, the other by absorption in the solution under examination. Wave lengths of the match points were computed by means of the Hartmann interpolation formula.

Solvents: Whenever the compounds were sufficiently soluble, absolute alcohol was used, but occasionally it was found necessary to use chloroform or dioxane. The chloroform used was of B.P. quality and the dioxane was purified by the method of Weissberger and Prosskauer.

Compounds: These were principally specimens prepared and used for investigations already published (Mellor and Craig, 1940; Mellor, 1941). Any compounds made specially for the work were analysed for the metal content as a check on their purity.

Magnetic Measurements: Data for most of the compounds studied have been already published. Measurements for two compounds not previously given are set out below:

Bis-1-hydroxyacridine nickel:

$$\chi = 8.27 \times 10^{-6}; \psi_M = 3,700; \psi_A = 3,924 (294^\circ); \mu = 3.04 \text{ B.M.}$$

Bis-thiolquinoline nickel:

$$\chi = 11.57; \psi_M = 4,380; \psi_A = 4,570 (293^\circ); \mu = 3.17 \text{ B.M.}$$

Except where indicated, magnetic measurements were made exclusively on solids.

EXPERIMENTAL RESULTS.

The results of an examination of a limited number of compounds of Classes I and II have already been briefly reported (Mills and Mellor, 1941) and the extension of the survey to the remaining classes has served to confirm and to enable elaboration of the earlier findings. The principal features which emerge from the full survey are these: in paramagnetic complexes the nickel atom, as a rule¹ makes very little contribution to the absorption spectrum; in other words, there is little difference between the absorption spectrum of the metal complex and that of the chelate molecule from which it is derived. The curves for acetyl acetone and bis-acetyl acetone nickel (Fig. 1) illustrate this point. (See also Fig. 2.) On the other hand, with diamagnetic complexes it has been found that, in general, the presence of the nickel atom can be associated with the appearance of a broad band of considerable intensity, the molecular extinction coefficient at the maximum of which ranges from 3,000 to 12,000 or more. This band, referred to in the sequel as the nickel band, is to be clearly seen in Figs. 3-7, which show curves for some of the compounds examined. Data concerning the position of the maximum of the nickel band (λ_{\max}) and the molecular extinction coefficient at the maximum (ϵ_{\max}) for the diamagnetic nickel complexes are summarised in Table I.

DISCUSSION.

Diamagnetic Complexes.

It will be seen from Table I that the position and intensity of the nickel band maximum varies from compound to compound, a point which is perhaps more clearly brought out in Fig. 8, showing the band as it appears in a number of different compounds. There is little evidence that the electronegativity² of the four atoms attached to nickel exercises any marked influence on the position³ of the band maximum (see curves II, III, IV and V, Fig. 8) since the variation in position for compounds within a class (Class II, curves I and II, Fig. 8) is greater than the variations between the classes; nor does it seem that the electronegativity of these four atoms produces any regular effect on the intensities of the bands as judged, either by the extinction coefficient at the band maximum or more appropriately, by the band areas. Since the nickel band becomes vanishingly weak in ionic complexes where electronegativity differences between nickel and the atoms attached to it are greatest, it was at first believed that a study of the effect of electronegativity differences might be a promising line of investigation. The electronegativity differences between

the attached atoms and nickel are least in Class V $\begin{array}{c} \text{S} \backslash \quad / \text{S} \\ \text{Ni} \\ \text{S} / \quad \backslash \text{S} \end{array}$ but it will be seen

from Fig. 8 that, for the one Class V compound studied, the intensity, instead of being greatest, is the least of all. In varying the kind of atom bound to nickel, large changes are simultaneously brought about in the remainder of the molecule and there seems little hope of disentangling the effects produced by these variations on the absorption of light, from absorption effects produced by concomitant changes in the remainder of the molecule. The introduction of a nickel atom into a chelate molecule causes the bands of the chelate molecule (or molecules) to undergo some change, usually a bathochromic shift. The curves for salicylaldehyde-propylene-diamine and its nickel derivative (Fig. 5) may be taken as an illustration of what happens to the chelate bands. The

¹ The one exception to this rule will be referred to in the discussion.

² The electronegativities of O, N and S as defined by Pauling are 3.5, 3.0 and 2.5 respectively.

³ The bands are sufficiently symmetrical to enable the use of the position of the band maximum to describe the position of the band itself.

TABLE I.
The Position and Intensity of the Nickel Band.*

Compound.	Formula.	Solvent.	$\epsilon_{\max} \times 10^{-3}$.	λ_{\max} .
<i>Class II.</i>				
Bis-o-aminophenol-nickel ..	$(\text{O.C}_6\text{H}_4\text{NH}_2)_2\text{Ni}$	Absolute alcohol.	2	432
Bis-iminopaonol-nickel	$(\text{O}-\text{C}_6\text{H}_4\text{CH}_2\text{O.CH:NH})_2\text{Ni}$	Absolute alcohol and dioxane.	5	394
Bis - salicylaldehyde - propylene diamine nickel.	$(\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2)_2\text{Ni}$	Absolute alcohol.	6	405
Bis - salicylaldehyde - ethylene-diamine nickel.	$(\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2)_2\text{Ni}$	Absolute alcohol.	6	405
Bis-salicylaldimine-nickel ..	$(\text{O}-\text{C}_6\text{H}_4\text{CH:NH})_2\text{Ni}$	Absolute alcohol.	4	405
Bis - N - methyl - salicylaldimine nickel.	$(\text{O.C}_6\text{H}_4\text{CH.N.CH}_3)_2\text{Ni}$	Absolute alcohol.	?	400
Bis - o - hydroxyacetophenone imine nickel.	$(-\text{O}-\text{C}_6\text{H}_4\text{C.CH}_3\text{:NH})_2\text{Ni}$	Dioxane.	5	411
Bis - nicotinylacetone - ethylene-diamine nickel.	$(\text{C}_{20}\text{H}_{16}\text{O}_2\text{N}_2)_2\text{NiH}_2\text{O}$	Absolute alcohol.	7	405
Bis - acetylacetone - ethylene-diamine nickel.	$(\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2)_2\text{Ni}$	Absolute alcohol.	6	385
Bis - benzene - azo β naphthol nickel.	$(-\text{O.C}_{10}\text{H}_7\text{N:N.C}_6\text{H}_4)_2\text{Ni}$	Chloroform	$\sim 12\frac{1}{2}$ (by analysis)	~ 400
Bis-salicylaldoxime nickel ..	$(-\text{O}-\text{C}_6\text{H}_4\text{CH:N.OH})_2\text{Ni}$	Absolute alcohol.	8 (Very weak)	385 620
Bis - formylcamphorethylene - diamine nickel.	$(\text{C}_{14}\text{H}_{14}\text{O}_2\text{N}_2)_2\text{Ni:3H}_2\text{O}$	Absolute alcohol.	0.012†	385 620
<i>Class III.</i>				
Bis- α -benzildioxime nickel ..	$(\text{C}_6\text{H}_5\text{C:NO.C.NO.H.C}_6\text{H}_5)_2\text{Ni}$	Absolute alcohol.	12.5	405
Bis - 44' - dimethyldiazo - amino - benzene nickel.	$(\text{CH}_3\text{C}_6\text{H}_4\text{.NH.N:N.C}_6\text{H}_4\text{.CH}_3)_2\text{Ni}$	Dioxane.	N1	400
1 : 8 naphthalene diamine nickel sulphate.	$[\text{Ni}(\text{C}_{10}\text{H}_7\text{.NH}_2\text{.NH}_2)_2]\text{SO}_4$	Dioxane.	1.8	390
<i>Class IV.</i>				
Bis-thiosemicarbazide nickel ..	$(\text{NH}_2\text{.CS.N.NH}_2)_2\text{Ni}$	Propylene glycol.	4	405
<i>Class V.</i>				
Bis-xanthic acid nickel ..	$(\text{S.CS.OC}_2\text{H}_5)_2\text{Ni}$	Absolute alcohol.	3	415

* The concentration of the solutions used varied from around 0.001 M to 0.0001 M. Some of the absorption curves (Figs. 1-12) have been constructed from data for solutions at two or even three different concentrations.

† This second weaker band has been found only in green diamagnetic complexes.

‡ Owing to the empirical nature of the process used to analyse these curves these results are approximate only.

two strong bands shown thus --- in Fig. 5 are presumably the x and y bands (Lewis and Calvin, 1940); both are shifted to the red in the nickel derivative. Although a bathochromic shift is what generally happens, two examples of the opposite (hypsochromic) shift have been observed with nicotinylacetone-ethylene-diamine and acetylacetone-ethylenediamine nickel.

As a rule, the nickel band stands out clearly, but there are occasions when it is partly or wholly obscured by strong absorption of the chelate molecule itself in the same region of the spectrum. This is to be seen in the complexes of benzene-azo- β -naphthol and diazoaminobenzene. Let us first consider the case of benzene-azo- β -naphthol whose absorption in chloroform solution is shown in Fig. 9. This curve exhibits two maxima at 485 and 311 m μ respectively.

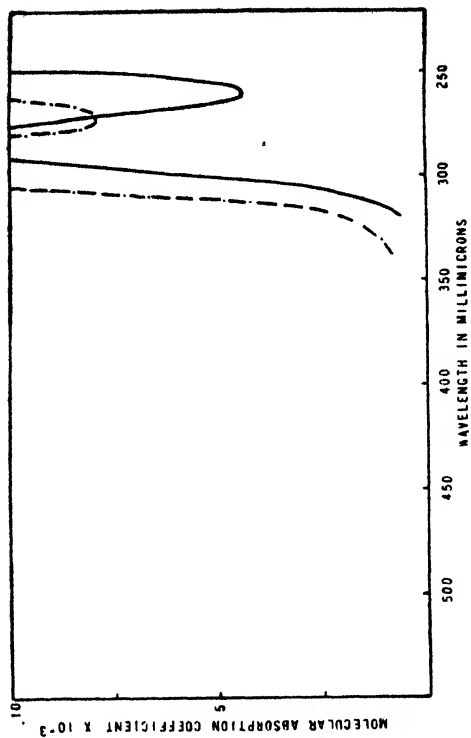


Fig. 2.

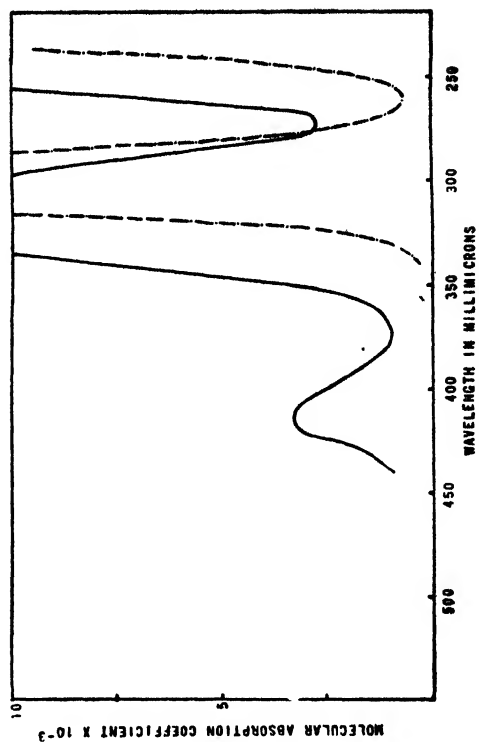


Fig. 4.

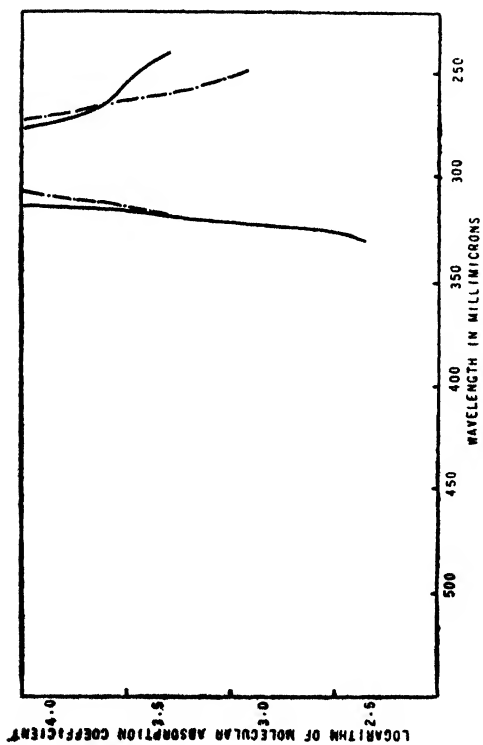


Fig. 1.

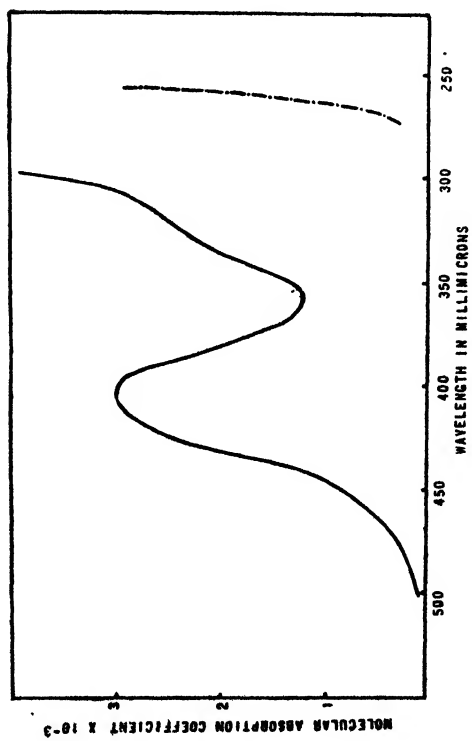


Fig. 3.

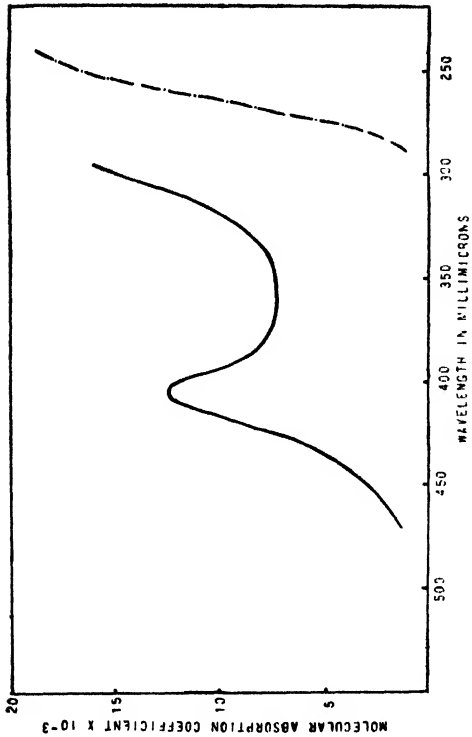


Fig. 6.

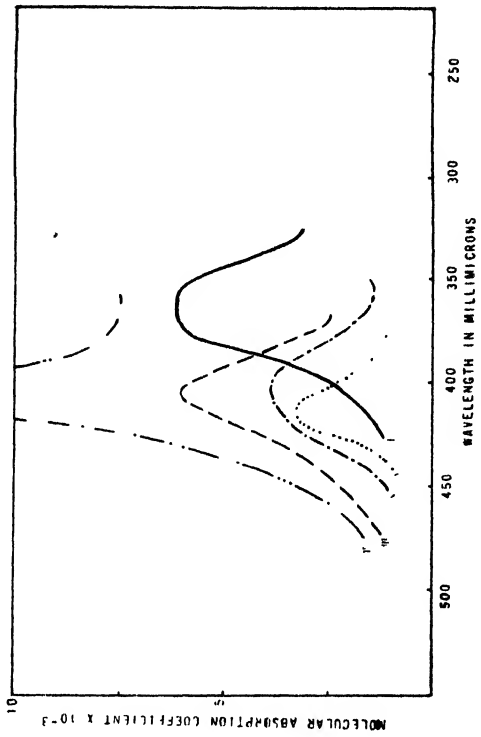


Fig. 8.

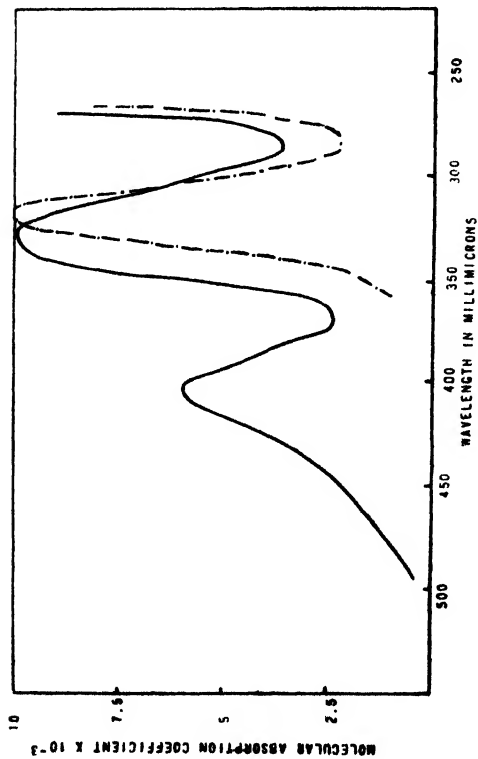


Fig. 5.

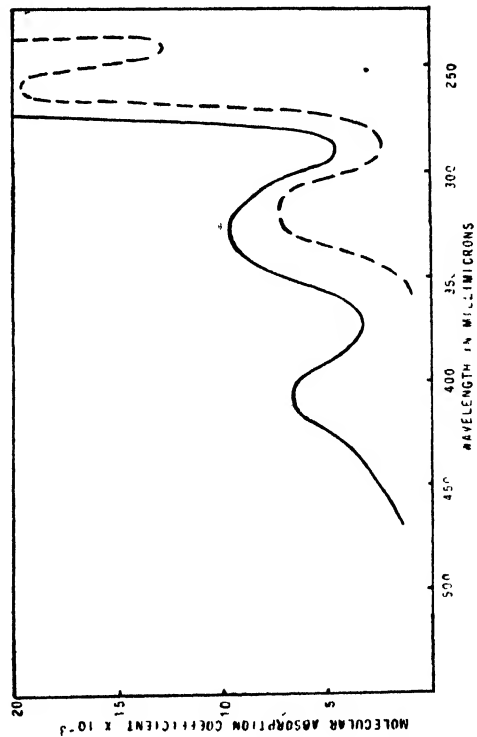


Fig. 7.

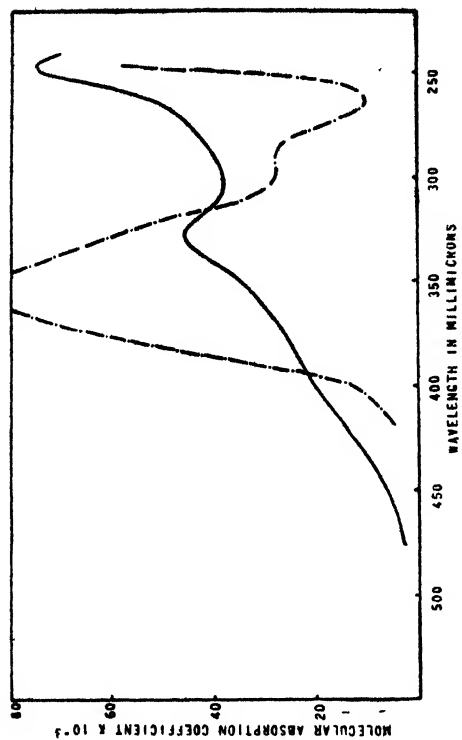


Fig. 10.

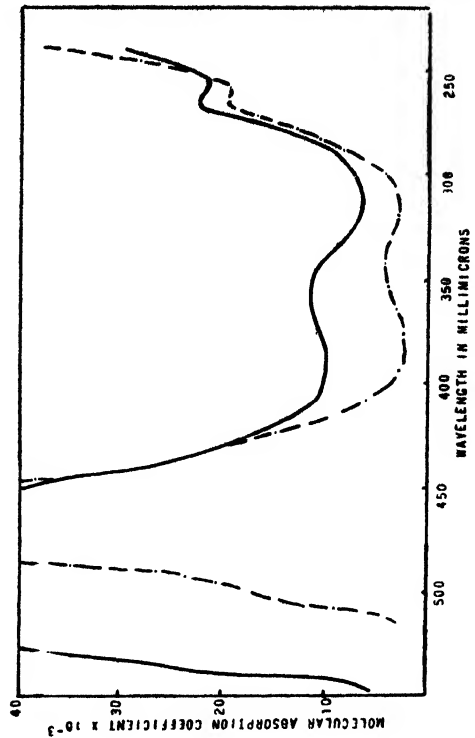


Fig. 12.

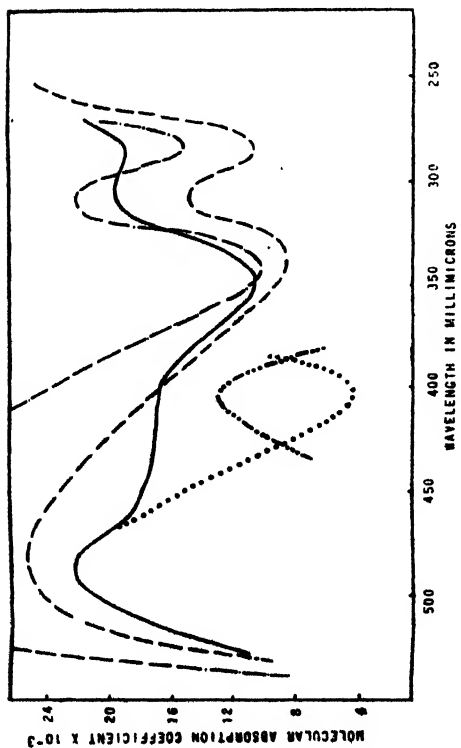


Fig. 9.

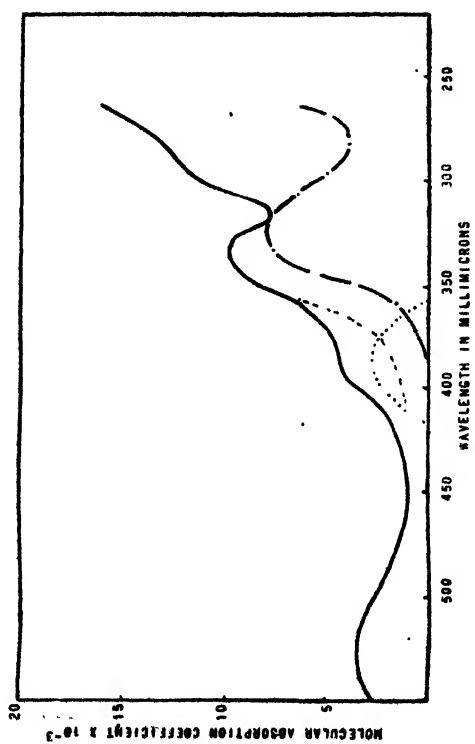


Fig. 11.

The chloroform solution of the corresponding nickel complex (Fig. 9) shows maxima at 486 and 307 $m\mu$; a significant feature of this last absorption curve is the inflexion between 400 and 450 $m\mu$. If the 486 $m\mu$ band of the nickel complex is continued down parallel to the corresponding band of the chelate (this is identified on the assumption of a hypochromic shift) and the ordinates of this curve are subtracted from those of that part of the curve of the nickel complex lying between 350 $m\mu$, a curve is obtained which suggests that the inflection is due to the super-position of two bands in this region. There is little doubt that the curve shown thus — · · · — · · · represents the nickel band. On attempting to apply similar treatment to the curves of diazoaminobenzene, 44'-dimethyl-diazoaminobenzene and the corresponding nickel complexes, difficulties are met with owing to the complexity of the effects produced in the bands of the chelates themselves which, as a result of the formation of the metal complexes, are considerably changed in contour as well as in position. The curves for diazoaminobenzene and its nickel derivative are shown in Fig. 10.

Paramagnetic Complexes.

The following paramagnetic complexes were examined: Class I (a) bis-acetylacetone nickel (Fig. 1), (b) bis-salicylaldehyde nickel, (c) bis-formylcamphor nickel; Class II (d) bis-1-hydroxyacridine nickel, (e) bis-8-hydroxyquinoline

EXPLANATION OF FIGURES.

- Fig. 1.—Acetylacetone (2ϵ) in 0.01 alcoholic NaOH: — · —
 Bis-acetylacetone nickel in absolute alcohol: — — —
- Fig. 2.— α -Phenylenediamine (2ϵ) in chloroform: — · —
 Bis-phenylenediamine nickel sulphate in water: — — —
- Fig. 3.—Thiosemicarbazide (2ϵ) in water: — · —
 Bis-thiosemicarbazide nickel in propylene glycol: — — —
- Fig. 4.—Potassium ethyl xanthate (2ϵ) in absolute alcohol: — — —
 Bis-xanthic acid nickel in absolute alcohol: — — —
- Fig. 5.—Bis-salicylaldehyde-propylenediamine in absolute alcohol: — · —
 Bis-salicylaldehyde propylenediamine nickel in absolute alcohol: — — —
- Fig. 6.— α -Benzildioxime (2ϵ) in chloroform: — · —
 Bis- α -benzildioxime nickel in absolute alcohol: — — —
- Fig. 7.—Bis-salicylaldehyde-ethylenediamine in absolute alcohol: — — —
 Bis-salicylaldehyde-ethylenediamine nickel in absolute alcohol: — — —
- Fig. 8.—The nickel band in different complexes.
 I. Bis-acetylacetone-ethylenediamine nickel (alcohol): — — —
 II. Bis-salicylaldehyde-propylenediamine nickel (alcohol): — — —
 III. Bis- α -benzildioxime nickel (chloroform): — · · · · ·
 IV. Bis-thiosemicarbazide nickel (propylene glycol): — · — · —
 V. Bis-xanthic acid nickel (alcohol): · · · · ·
- Fig. 9.—Benzene-azo- β -naphthol (2ϵ) in absolute alcohol: — — —
 Benzene-azo- β -naphthol (2ϵ) in absolute chloroform: — · —
 Bis-benzene-azo- β -naphthol nickel in chloroform: — — —
 The nickel band (see text): — · · · · ·
- Fig. 10.—Diazoaminobenzene (4ϵ) in dioxane: — · — · —
 Tetrakis-diazoaminobenzene nickel in dioxane: — — —
- Fig. 11.—Thioquinoline (2ϵ) in chloroform: — · — · —
 Bis-thiolquinoline nickel in chloroform: — — —
 The nickel band: · · · · ·
- Fig. 12.—33': 55' Tetramethyl 44' dicarbethoxy-dipyrromethene (2ϵ) in alcohol: — · — · —
 Bis 33': 55' tetramethyl 44' dicarbethoxy-dipyrromethene nickel in alcohol: — — —

nickel,⁴ (f) salazine nickel, (g) bis-glycine-nickel, (h) bis-orthophenylenediamine nickel sulphate (Fig. 2), and (i) 3 3': 5 5' tetramethyl 4:4' dicarbethoxy-dipyrromethene nickel.⁵ The absorption curves of these complexes appear to be essentially those of the chelate molecules with the bands displaced to longer wave-lengths and broadened. An interesting feature of the curves is that, in the two instances examined, (a) and (e), the absorption bands of the nickel complexes in alcohol solution bear a strong resemblance to the bands of the chelate molecule in alcoholic sodium hydroxide. (See Fig. 1.) Although no strong nickel band was observed in any of the above complexes, there was some evidence of the presence, in the more soluble complexes, of a very weak band in the 400 m μ region. Such a band ($2\epsilon_{\max} \sim 10$) was found at 375 m μ with nickel glycine whose solubility in water is sufficiently great to permit the investigation of the band. Similar very weak bands have been observed with aqueous solutions of simple nickel salts which are also paramagnetic. Datta and Deb (1935), for example, have reported that nickel chloride shows a weak band ($\epsilon_{\max} \sim 10$) with a maximum at 407 m μ . In ethyl alcohol, the band maximum is shifted to 420 m μ and in concentrated hydrochloric acid to 430 m μ . More recently, Tréhin (1943) has studied the absorption of nickel sulphate, both in the solid state and in solution; for the former he finds a maximum at 389 m μ and for the latter a maximum at 395 m μ . Extinction coefficients are not stated in the abstract of this paper which is the only form in which it is available at present. Bjerrum (1941) reports a very weak band ($\epsilon_{\max} \sim 1$) at 680 m μ for the hexaquo nickel ion. The fact that these maxima are located in the same regions of the spectrum as the stronger nickel bands of the diamagnetic complexes suggests that the bands, both strong and weak, have similar origins. In other words, if this assumption is correct, the effect of lowering the magnetic moment of the nickel atom is to enhance enormously its absorption of light in the 400 m μ region of the spectrum. As to why reduction in moment should produce this effect, no explanation can, as yet, be advanced. There are, however, certain departures from the general rule which suggest the course of further investigation.

ANOMALIES.

Paramagnetic Compounds.

Perhaps the most puzzling anomaly is offered by bis-thiolquinoline nickel, whose moment (3.17 Bohr magnetons) has been checked on several occasions.⁶ Reexamination of the absorption spectrum which is shown in Fig. 11 also failed to remove the anomaly. Analysis of the absorption curve obtained with a chloroform solution, along the lines used with benzene azo- β -naphthol nickel, indicates the presence of a band with a maximum at about 390 m μ .

Diamagnetic Compounds.

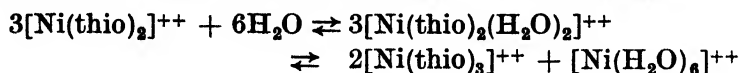
Although the enhanced nickel band is produced by bis-thiosemicarbazide nickel, it is absent from the absorption of aqueous solutions of bis-thiosemi-

⁴ The absorption spectrum of 8-hydroxyquinoline in alcoholic sodium hydroxide has been described by Fox (1910).

⁵ This compound is of special interest since it is considered to owe its paramagnetism to steric effects which force normally co-planar Ni-N bonds to adopt a tetrahedral configuration. The absorption spectra of the metal complex and the chelate from which it is derived are shown in Fig. 12. Although there is an increase in the absorption in the 400 m μ region, there seems to be no new maximum which can be attributed to the nickel atom.

⁶ We are indebted to Mr. J. B. Willis for checking the measurements on this compound. Jensen (1936) states that the compound is diamagnetic, but we are unable to confirm this.

carbazine nickel nitrate (Fig. 3) which, in the solid state, is diamagnetic.⁷ There are reasons for believing (Jensen, Rancke-Madsen, 1934) that in aqueous solution there is an equilibrium between square and octahedral complexes formed by the coordination of two water molecules or a third semicarbazide molecule :



It was found that Beer's Law does not hold for aqueous solutions of bis-thio-semicarbazide nickel nitrate, which fact is consistent with Jensen's interpretation of the behaviour of these solutions. The absence of the nickel band from the absorption of these solutions must mean that the equilibrium is very largely in favour of the hexaquo and tris-thiosemicarbazide nickel ions. A consideration of the anomalous behaviour of solutions of bis-thiosemicarbazide nickel nitrate naturally raises the question as to whether the magnetic condition of the metal complexes should not have been studied in solution as well as in the solid state. Owing to the low solubility of many of the compounds and also to the fact that no microbalance was available for the magnetic measurements, attention was confined, in the present work, to solids. It is clear, however, that susceptibility measurements should be extended to solutions with aid of a Curie-Chéneveau or a more sensitive Gouy balance. Even with the more sensitive equipment, the low solubility of many internal nickel complexes may considerably restrict the field of investigation.

The need for further work on solutions is obvious from the work of French, Magee and Sheffield (1942), who report that in methyl alcohol, at a concentration not stated, ethylenediamine-formylcamphor nickel is weakly paramagnetic (1.9 Bohr magnetons). In the solid state, this compound is diamagnetic. Mr. W. A. Rawlinson, of the Walter and Eliza Hall Institute of Research, Melbourne, has confirmed the observation of French *et al* (1942), although the observed moment was somewhat lower at the particular concentration he studied. He has also extended measurements to chloroform solutions and has found similar behaviour. On the assumption that the moment of Ni^{++} must be either zero or in the neighbourhood of 2.8 Bohr magnetons, there is, in these solutions, an equilibrium between dia- and paramagnetic molecules with the equilibrium in favour of the former.⁸ Under these circumstances it may be questioned whether Beer's Law is applicable to solutions like those of ethylenediamine-formylcamphor nickel. Tests for the validity of the law for solutions of a few diamagnetic nickel complexes have been made over a rather limited range of concentrations and the law has been found to hold approximately (within the limits of experimental error of $\sim 2\%$). Plans are in hand for testing the applicability of Beer's Law to ethylenediamineformylcamphor nickel and similar substances over as wide a range as solubility restrictions permit; it is also hoped to discover whether there is any variation of paramagnetic susceptibility over the same concentration ranges.

SUMMARY.

It has been found that with paramagnetic nickel complexes the metal atom, as a rule, makes very little contribution to the absorption spectrum. On the other hand, nickel complexes which, in the solid state are diamagnetic, form solutions whose absorption spectra are characterised by the appearance of a

⁷ Moniminobiuret nickel, which is diamagnetic in the solid state, also fails to show any evidence of the nickel band when dissolved either in alcohol or propylene-glycol. No explanation can, as yet, be given for the anomalous behaviour of this substance.

⁸ Variations in the position of this equilibrium from compound to compound may have some influence on the intensity (area) of the nickel band. On the other hand, the above assumption may not be correct—all the nickel atoms may have moments of 1.9 Bohr magnetons.

broad band of considerable intensity. This band can be associated with the presence of the nickel atom in the complex. Several deviations from these rules have been noted, but in only one instance has the exceptional behaviour been explained.

ACKNOWLEDGMENTS.

We are indebted to Mr. W. A. Rawlinson for magnetic measurements on solutions of nickel-ethylenediamine-formylcamphor; to Mr. F. P. Dwyer for specimens of nickel triazene compounds and finally to Dr. R. Lemberg for making available facilities for visual work, with the Hilger-Nutting spectrophotometer.

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BESSEL'S FORMULA IN RELATION TO THE CALCULATION OF THE PROBABLE ERROR FROM A SMALL NUMBER OF OBSERVATIONS.

By R. C. L. BOSWORTH, Ph.D., F.A.C.I.

Manuscript received, July 4, 1944. Read (in title), August 2, 1944.

The probable error (s) from a group of observations x_1 , n in number with a mean at \bar{x} calculated from Bessel's formula, viz.

$$s = 0.6745 \sqrt{\frac{\sum(\bar{x} - x_1)^2}{n-1}} \dots\dots\dots (1)$$

is known to be an underestimate.

Jeffreys (1932), basing his theory on the lemma that the prior probability for the precision factor lying in the range h to $h+dh$ is proportional to

$$\frac{1}{h}dh$$

has shown that the probable error can be represented by an expression of the type

$$s = U \sqrt{\frac{\sum(\bar{x} - x_1)^2}{n-1}} \dots\dots\dots (2)$$

where the coefficient U varies with n . Some values of U given by Jeffreys are reproduced in Table I.

TABLE I.
Coefficients given by Jeffreys.

n	U
2	1.000
3	0.816
4	0.766
5	0.740
6	0.728
7	0.718
10	0.703
∞	0.674

If now we assume that equation (2) can approximately be replaced by

$$s = 0.6745 \sqrt{\frac{\sum(\bar{x} - x_1)^2}{n-1-a}} \dots\dots\dots (3)$$

which is Bessel's equation with a small correcting factor a , we must have approximate equality between

$$\frac{(0.674)^2}{U^2} \quad \text{and} \quad \frac{n-1-a}{n-1}$$

$$\frac{0.455}{U^2} = 1 - \frac{a}{n-1}$$

or

Figure 1 shows $\frac{1}{U^2}$ plotted against $\frac{1}{n-1}$.

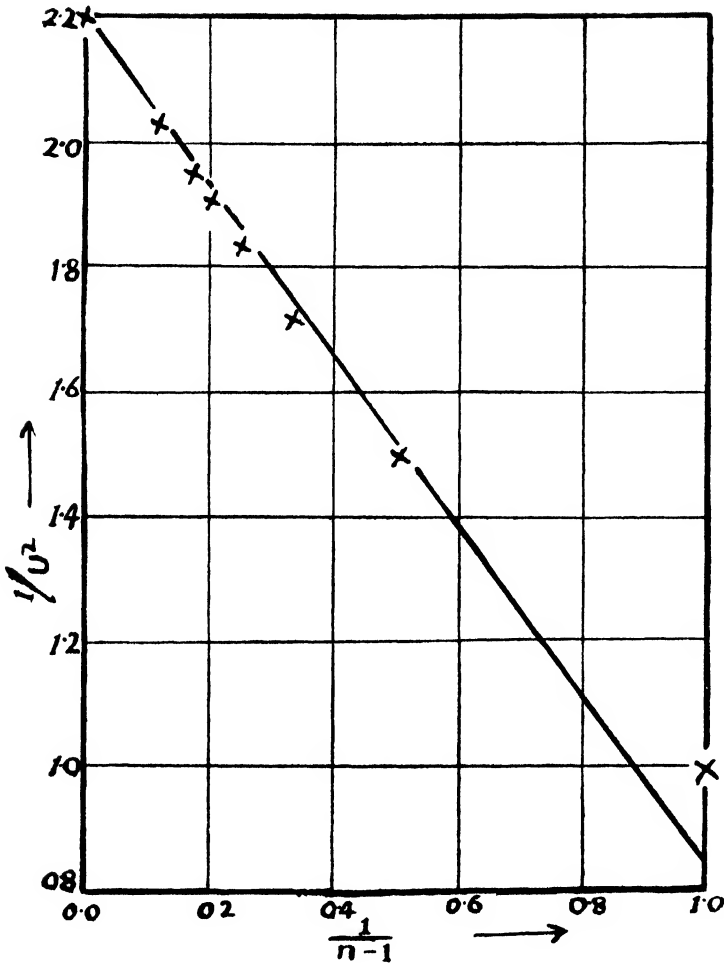


Fig. 1.

The figure shows that with the exception of the point referring to the sample of two observations only, the points fall very satisfactorily on the straight line

$$\frac{0.455}{U^2} = 1 - \frac{0.63}{n-1}$$

Consequently we have as an improved form of Bessel's equation

$$s = 0.6745 \sqrt{\frac{\sum(\bar{x} - x_1)}{n-1.63}} \dots\dots\dots (4)$$

The error incurred in using this approximation as compared with Bessel's equation is given in Table II for a number of different sample sizes.

TABLE II.

A Comparison of the Errors involved in Equation (4) with Bessel's Equation.

Number of Observations.	Error in Equation (4).	Error in Bessel's Equation.
2	11.0%	48.0%
3	0.1%	21.0%
4	0.9%	14.0%
6	0.8%	8.0%
10	0.5%	4.0%
∞	0.0%	0.0%

It will be noted that the trifling modification involved in the change from equation (1) to equation (4) results in a great increase in the accuracy of the expression when applied to small numbers of observations in all cases except that of two observations only, in which case the significance of estimated error is very low anyhow. Applied to large numbers of observations equation (4) is not significantly different from equation (1). For these reasons it is suggested that equation (4) is a more suitable expression for checking the accuracy of experimental results than the original Bessel's equation (equation (1)).

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REVIEW OF ANALYSES OF SOME AUSTRALIAN FLEECE WOOLS.

By M. LIPSON, B.Sc., A.A.C.I.,
and UNA A. F. BLACK, B.Sc.

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INTRODUCTION.

The presence in the fleece of constituents other than wool is realised by scientific workers and wool valuers. Methods for the quantitative division of the fleece into six major constituents, namely wool wax¹ (lanolin), suint, dirt, moisture, vegetable material and wool fibre, have been previously described. In the commercial evaluation of any greasy wool sample, one essential is a knowledge of its content of pure wool fibre, which naturally depends upon the amounts of the other five constituents present. The work outlined in Section A of the paper was undertaken to gain some idea of the variations that can occur in the fleece as it comes to the market and to determine the effect each may have on yield.

The results cover about 200 analyses of different types of wools appraised during 1941 to 1944. Most of the samples were from the N.S.W. clip, but some were from South Australia, Western Australia, Queensland and Victoria.

In biological studies concerned with the secretion of wax and suint by the sheep, it is desirable to express the results for each constituent as percentages on the oven-dry clean wool weight. This procedure presents a clearer picture of the relative amounts of wax, suint and wool produced by the sheep than is shown by percentages based upon fleece weights which would be affected by extraneous dirt and vegetable material. In the present work, however, we are mainly concerned with the actual percentage composition of the fleece, irrespective of whether the constituents are natural or extraneous materials. The results are therefore in general expressed as percentages on the fleece weight, although ratios for wax and suint (percentages on oven-dry clean wool weight) are included as a matter of interest.

The bulk of the N.S.W. clip is merino fleece wool, and this constitutes the major group studied. Cross-bred fleece wools have also been examined as well as black wool, fellmongered wool and "canary stained" wool from the Kimberley district of Western Australia.

In addition to the investigations outlined above, experiments have been carried out to find the basis of certain terms used by wool valuers in their description of the greasy fleece. A discussion of this work appears in Section B of this paper and includes results of observations on greasy wools described by the practical man as "oily", "dry", "gritty", "earthy", etc.

SECTION A. QUANTITATIVE VARIATIONS OF FLEECE CONSTITUENTS.

1. Experimental Procedure.

The samples for analysis usually weighed about 15–25 gm., and were obtained by carefully sub-sampling larger samples of 6–8 lb., which had been drawn from the wools as they appeared

¹ The term "fat" is often applied to the ether-soluble fraction of the fleece, but this is incorrect, as there are no glycerol esters present.

for appraisement in the wool stores.² By comparing the oven-dry yields of pure wool in these small samples with those obtained from larger samples scoured in the testing house it was shown that with careful drawing they were representative of the lots from which they were selected. The method of fleece analysis was essentially that described by Freney (1940). Wax was removed by four hours' extraction with redistilled petroleum ether, and suint by extraction with distilled water at room temperature. The dirt remaining in the wool after wax and suint extraction was estimated by weighing the oven-dry wool before and after a mild soap and soda ash scour. The loss in weight added to the weight of the dirt which was collected by filtration of the suint extract gave the total dirt content. Moisture content of the fleece was found by drawing another small sample at the same time as the first and finding the loss in weight on drying at 100–105° C. for four hours.

The results of this work have been set out in Tables I to VIII.

To facilitate the interpretation of these results, Table IX contains the range and average value for each constituent in the different groups of fleeces.

TABLE I.

Fleece Constituents of Merino Types 70's and Up.

Sample No.	District.	Wax.		Suint.		Dirt Per Cent.	Moisture Per Cent.	Oven-Dry Wool Per Cent.	Quality.	Length.
		Per Cent.	Ratio.	Per Cent.	Ratio.					
2706	Armidale	20.4	35.2	3.5	6.0	10.5		58.0	90's and up	Good. (Minimum 27")
2715	Armidale	19.7	33.3	4.9	8.3	6.9		59.1	90's and up	
6073	Yass	22.4	39.7	3.3	5.9	9.9	8.3	56.5	90's and up	
6074	Yass	15.2	25.1	2.0	3.3	11.6	8.1	60.6	70's and up	
6423	Yass	17.5	27.6	2.1	3.3	8.0	9.0	63.5	70's and up	
1539	Barraba	19.9	39.0	9.4	18.4	8.5		51.0	80's and up	
1288	Wanaaring	17.5	42.5	8.1	19.7	25.6		41.1	70's and up	
124		18.8	40.3	3.8	8.1	21.2		46.7	70's and up	Irregular.
125		18.7	41.7	4.9	10.9	22.7		44.8	70's and up	
5821	Longreach, Q.	14.2	28.2	7.2	14.3	18.3	9.4	50.3	70's and up	
5890	Julia Creek, Q.	13.2	26.0	7.6	15.0	19.5	9.1	50.8	70's and up	
3320	Wanaaring	16.0	44.0	7.9	21.7	34.8		36.4	70's and up	
1360	Brewarrina	14.2	35.8	7.1	18.4	29.0		38.6	74's and up	
1361	Brewarrina	14.8	40.3	5.5	15.0	35.2		36.7	74's and up	
1341	Bourke	14.0	47.6	7.0	23.8	43.8		29.4	70's and up	
6172	Inverell	17.5	29.6	4.2	7.1	8.0	10.7	59.1	70's and up	Short.
1239	Bourke	17.4	42.0	4.6	11.1	28.1		41.5	74's and up	
1401		18.8	36.0	5.5	10.5	12.8		52.2	70's and up	
107		14.8	28.4	3.8	7.3	19.2		52.2	70's and up	
2645	Braidwood	25.4	59.8	4.9	11.5	21.4		42.5	70's and up	

TABLE II.

Fleece Constituents of Merino Type 64/70's.

Sample No.	District.	Wax.		Suint.		Dirt Per Cent.	Moisture Per Cent.	Oven-Dry Wool Per Cent.	Length.
		Per Cent.	Ratio.	Per Cent.	Ratio.				
2377	Uralla	22.2	41.1	5.1	9.5	9.4		54.0	Good. (Minimum 37")
5266	Manilla	19.9	33.8	3.9	6.6	7.9		59.0	
1334	Bourke	13.9	31.0	4.9	11.0	27.2		44.8	
652	Wyalinda	17.0	32.7	6.0	11.5	17.9		52.0	
6196	Stockinbingal	18.4	35.3	4.7	9.0	13.8	10.3	52.1	
3826	Bourke	16.6	44.6	5.6	15.1	33.8		37.2	
3429	Bourke	13.4	30.3	6.4	14.5	28.0		44.2	
3319	Wanaaring	12.7	27.8	5.4	11.8	28.4		45.7	
1675		18.5	42.0	5.4	12.3	25.0	9.4	44.0	

² The samples represented quantities of wool which varied from one to 62 bales, averaging 10 bales.

TABLE II.—Continued.

Fleece Constituents of Merino Type 64/70's.—Continued.

Sample No.	District.	Wat.		Suint.		Dirt Per Cent.	Moisture Per Cent.	Oven-Dry Wool Per Cent.	Length.
		Per Cent.	Ratio.	Per Cent.	Ratio.				
5904	Isisford, Q. . .	14.6	27.7	7.3	13.8	16.1	9.3	52.8	Irregular.
5909	Dirranbandi, Q. .	13.1	22.8	4.9	8.5	15.5	8.7	57.6	
5815	Tambo, Q. . .	12.8	24.2	4.3	8.1	20.8	8.7	53.0	
5872	Blackall, Q. . .	13.3	26.5	7.1	14.1	20.8	8.3	50.2	
5892	Morven, Q. . .	17.5	32.0	5.8	10.6	13.9	8.3	54.6	
5893	Morven, Q. . .	16.7	31.1	4.9	9.1	15.0	9.1	53.6	
1128	Wee Waa . . .	15.3	28.7	8.8	16.5	12.7		53.3	
1069	Bourke . . .	16.5	38.3	6.9	16.0	25.9		43.1	
178	Narrabri . . .	14.3	26.5	7.3	13.5	13.9		54.0	
3238	Bundarra . . .	15.7	25.2	4.2	6.7	8.2		62.3	
3835	Brewarrina . .	21.0	52.4	4.3	10.7	27.8		40.1	
2322	Bourke . . .	14.0	40.5	3.8	11.0	38.9		34.6	
3422	Wanaaring . .	15.6	38.9	4.8	12.0	31.6		40.1	
1238	Bourke . . .	13.3	28.2	6.3	13.4	24.2		47.1	
1243	Bourke . . .	14.1	29.7	5.1	10.7	21.0		47.5	
1310	Murrurundi . .	12.6	19.9	6.7	10.6	11.9		63.4	
1283	Wanaaring . .	13.7	30.7	8.6	19.3	24.8		44.6	
1296	Wanaaring . .	18.5	42.8	6.3	14.6	28.1		43.2	
1228	Bourke . . .	11.4	27.0	6.6	15.6	31.3		42.3	
1381	Bourke . . .	15.2	31.8	6.6	13.8	22.0		47.9	
653	Upper Murray, Vic. . .	14.6	23.1	4.1	6.5	7.2	10.3	63.2	Short.
1129	Wee Waa . . .	20.5	45.8	7.8	17.4	17.1		44.8	
3456	Bourke . . .	15.2	40.0	6.7	17.6	32.4		38.0	
1280	Wanaaring . .	16.2	37.0	7.1	16.2	24.9		43.8	
5233	—, W.A. . . .	12.5	28.3	11.1	25.1	21.8	11.8	44.2	
3324	Wanaaring . .	15.0	32.6	6.3	13.7	25.6		46.1	
3325	Wanaaring . .	14.0	30.4	7.6	16.5	25.3		46.1	
1282	Wanaaring . .	21.0	70.0	6.4	21.3	29.5		30.0	

TABLE III.

Fleece Constituents of Merino Type 64's.

Sample No.	District.	Wax.		Suint.		Dirt Per Cent.	Moisture Per Cent.	Oven-Dry Wool Per Cent.	Length.
		Per Cent.	Ratio.	Per Cent.	Ratio.				
3834	Brewarrina . .	17.5	39.6	4.9	11.1	27.7		44.3	Good (Minimum 3½")
1130	Wee Waa . . .	18.2	33.8	5.8	10.8	12.3		53.9	
1242	Bourke . . .	16.3	39.8	9.4	23.0	25.6		41.0	
1429	Bigga	20.5	34.8	4.6	7.8	7.4	9.0	59.0	Irregular
1493	Bookaloo, S.A. .	14.0	33.8	6.5	15.7	30.1		41.5	
1109	Inverell . . .	15.5	25.4	3.2	5.2	9.8		61.2	
1496	Sth. Hills, S.A. .	14.5	34.8	6.0	14.4	24.8		41.7	
1497	—, S.A. . . .	15.2	40.0	4.0	10.5	34.4		38.0	
1425	Wanaaring . .	13.9	31.0	5.3	11.8	27.6		44.8	
446	Wanaaring . .	15.3	34.2	7.7	17.2	24.1		44.8	
453	Wanaaring . .	15.8	34.0	8.0	17.3	25.5		46.4	
1822	North East, S.A. .	17.9	46.4	8.4	21.8	23.4		38.6	Short
1626	Barraba . . .	14.0	22.1	5.5	8.7	7.6	9.7	63.4	
123	—	16.1	28.8	5.0	8.9	12.6		56.0	
1120	Berridale . . .	17.4	31.4	7.8	14.1	7.5		55.5	
1229	—, W.A. . . .	13.4	28.0	10.7	22.4	17.3	12.1	47.8	

TABLE IV.
Fleece Constituents of Merino Types 64/60's and 60's and Under.

Sample No.	District.	Wax.		Suint.		Dirt Per Cent.	Moisture Per Cent.	Oven-Dry Wool Per Cent.	Quality.	Length.
		Per Cent.	Ratio.	Per Cent.	Ratio.					
6221	Nundle	16.8	27.8	5.0	8.3	7.3	10.8	60.4	64/60's	Good (Minimum 34')
3500	—, S.A.	13.4	31.2	3.8	8.9	29.6		43.0	64/60's	
5602	Tenterfield	12.4	18.6	4.1	6.1	6.3	10.7	66.8	60's	
3498	Nth. East, S.A.	13.5	30.1	5.4	12.0	25.6		44.9	60/64's	
441	Wanaaring	15.1	33.3	5.6	12.3	24.4		45.4	60/64's	
3490	Nth. East, S.A.	10.0	23.4	4.5	10.5	32.6		42.7	60.58's	
5232	—, W.A.	10.8	19.9	10.8	19.9	12.6	12.6	54.2	60's and up	
3200	Singleton	14.5	23.5	3.9	6.3	8.9	9.7	61.8	60/64's	Irregular
3811	—, S.A.	16.0	36.6	5.7	13.0	25.3		43.8	64/60's	
3819	Fair Nth., S.A.	19.3	52.5	5.8	15.8	28.9		36.8	64/60's	
6174	Inverell	15.2	25.0	5.4	8.9	7.2	11.0	60.8	60/64's	
3115	Inverell	15.2	24.7	3.8	6.2	8.8		61.5	60's	
3494	Bookaloo, S.A.	15.7	33.2	5.2	11.0	20.8		47.4	60's	

TABLE V.
Fleece Constituents of Crossbred Types 58's to 60/64's.

Sample No.	District.	Wax.		Suint.		Dirt Per Cent.	Moisture Per Cent.	Oven-Dry Wool Per Cent.	Quality.	Style.
		Per Cent.	Ratio.	Per Cent.	Ratio.					
672	Holbrook	16.4	29.7	8.0	14.5	9.3	10.8	55.3	60/64's	Super
1705	Bathurst	19.3	35.8	8.0	14.8	9.6		54.0	60/64's	
1706	Bathurst	16.1	27.8	8.1	14.0	7.9		58.0	60's	
5837	Wheeo	15.0	25.6	6.6	11.2	7.5	12.3	58.7	60/58's	
1699	Breadalbane	9.7	15.4	8.7	13.8	7.1		63.0	58/60's	
5853	Crookwell	9.3	14.1	7.0	10.6	5.8	12.6	66.2	58's	
1564	Blayney	13.4	24.4	8.4	15.3	13.3		55.0	60/64's	Good
406	Albury	12.4	23.2	8.6	16.1	13.4	10.7	53.5	60's	
4645	Narrandera	11.2	19.8	5.8	10.3	12.0		56.6	58's	
1546		8.2	13.4	10.4	17.0	7.4		61.3	58's	
5840	Goulburn	12.9	21.4	5.7	9.5	10.1	11.1	60.4	60's	Average
6212	Uralla	13.1	21.9	7.3	12.2	8.6	11.1	59.8	58's	
662	Warialda	7.4	11.9	13.4	21.6	6.2		62.2	58's	
5787	West Wyalong	10.6	21.5	8.1	16.4	23.7	9.5	49.3	60.58's	

TABLE VI.
Fleece Constituents of Crossbred Types 32/36's to 56/58's.

Sample No.	District.	Wax.		Suint.		Dirt Per Cent.	Moisture Per Cent.	Oven-Dry Wool Per Cent.	Quality.	Style.
		Per Cent.	Ratio.	Per Cent.	Ratio.					
697	Breadalbane	7.9	12.2	8.9	13.7	7.0		65.0	58/56's	Super
357	West Buckley									
	(Vic.)	14.6	23.8	6.5	10.6	5.6	10.6	61.4	58/56's	
407	Albury	11.0	19.1	7.9	13.7	10.7	11.3	57.8	56/58's	
5838	Wheeo	9.9	15.3	7.0	10.8	6.1	12.2	64.9	56/58's	
1625	Galong	5.6	9.1	10.7	17.4	6.5		61.5	56's	
646	West Mortlake									
	(Vic.)	9.1	13.1	4.4	6.3	5.6	11.5	69.5	56/50's	
5801	Galong	6.8	10.2	8.6	12.9	7.2	11.2	66.6	56/46's	
5854	Crookwell	5.3	7.3	6.7	9.3	4.3	11.6	72.2	46's	
902*	Wangaratta (Vic.)	11.4	19.0	9.0	15.0	5.4	12.8	60.0	32/36's	Good
903*	Wangaratta (Vic.)	7.6	11.0	5.5	8.0	5.4	12.2	69.0	32/36's	
1563		9.2	15.3	9.4	15.6	9.2		60.1	58/56's	
1565	Blayney	9.3	14.5	8.7	13.6	6.5		64.0	58/56's	
4640	Narrandera	10.1	16.9	7.1	11.9	9.2		59.9	56/58's	
5698	Young	9.1	15.2	8.4	14.1	11.8	11.4	59.8	56's	
5836		7.8	12.6	10.3	16.7	6.5	14.2	61.8	56/50's	
5839	Wheeo	7.2	11.4	9.6	15.2	5.4	14.2	63.4	56/56's	
5844	Bungendore	7.2	11.0	8.9	13.6	6.5	12.1	65.6	56's	Average
5895	Mudgee	6.9	10.9	10.1	16.0	7.2	13.0	68.3	50/46's	
5786	Binalong	5.9	8.7	8.9	13.2	6.5	12.2	67.7	46/50's	
4647	Narrandera	12.4	23.4	7.4	14.0	13.1		53.0	56/58's	
0527	Exeter	6.8	10.3	7.4	11.2	7.4	12.6	66.0	56's	

* Lincoln wools.

TABLE VII.
Fleece Constituents of Feltmongered Wools.

Sample No.	District.	Wax.		Suint.		Dirt Per Cent.	Moisture Per Cent.	Oven-Dry Wool Per Cent.	Quality.	Minimum Length.
		Per Cent.	Ratio.	Per Cent.	Ratio.					
Merino										
3563	Queensland ..	20.0	39.5	0.1	0.2	19.0	7.9	50.6	64's up	3½"
3564	Queensland ..	16.0	25.8	0.1	0.2	10.6	9.5	62.1	64/70's	2½"
3566	Queensland ..	17.3	28.0	0.1	0.2	9.9	9.0	61.6	64's up	1½"
3853	N.S.W.	16.6	27.0	0.8	1.3	14.2	7.2	61.5	60/64's	3"
5441	N.S.W.	16.6	25.8	0.8	1.2	9.7	8.4	64.3	60/64's	3"
3220	N.S.W.	16.2	23.8	0.6	0.9	6.9	8.1	68.0	60/64's	1½"
*3565	Queensland ..	14.6	21.9	0.1	0.2	7.6	9.6	66.6	58/60's	2"
*3222	Queensland ..	9.9	14.1	0.4	0.6	10.3		70.0	58/56's	3½"
9289	N.S.W.	14.6	27.2	1.4	2.0	21.5	9.6	53.6	64's up	2½"
9259	Queensland ..	12.0	21.2	0.6	1.1	21.5	8.2	56.6	64/70's	2"
9260	Queensland ..	17.0	26.4	0.9	1.4	8.2	8.6	64.5	64/70's	2"
9261	Queensland ..	16.0	25.2	0.8	1.3	10.0	8.6	63.7	64/70's	1½"
9282	Queensland ..	18.5	30.0	0.9	1.5	10.6	9.0	61.5	64/70's	1½"
9203	Queensland ..	15.5	23.0	0.7	1.0	7.2	9.2	67.4	60/64's	2½"
9204	Queensland ..	14.4	21.3	0.5	0.7	8.6	9.2	67.6	60/64's	2½"
9265	Queensland ..	16.5	24.6	0.7	1.0	6.4	9.2	67.0	60/64's	2"
9267	Queensland ..	16.5	25.5	0.7	1.1	8.6	9.4	64.7	64/70's	2"

* Cross-bred type.

TABLE VIII.
Fleece Constituents of Some Black Wools.

Sample No.	Wax.		Suint.		Dirt Per Cent.	Moisture Per Cent.	Oven-Dry Wool Per Cent.	Type.
	Per Cent.	Ratio.	Per Cent.	Ratio.				
5672 ..	19.7	36.6	6.7	12.4	10.2	10.5	53.8	Merino
5676 ..	17.7	31.9	6.9	12.4	11.4	9.5	55.5	"
5677 ..	16.0	35.6	8.2	18.3	23.2	8.7	44.9	"
5685 ..	8.8	15.5	11.0	19.3	14.2	10.2	57.0	Crossbred

TABLE IX.
Average Values and Variations in Fleece Constituents.

Wool Per Cent.			Wax Per Cent.			Suint Per Cent.			Dirt Per Cent.			Moisture Per Cent.		
Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.
66.8	29.4	48.9	25.4	10.0	16.1	12.0	2.0	6.1	43.8	6.3	19.6	12.6	8.1	9.6
72.2	49.3	61.0	19.3	5.3	10.6	13.4	4.4	8.2	23.7	4.3	8.4	14.2	9.5	12.0
70.0	50.6	63.0	20.0	9.9	15.8	1.4	0.1	0.6	21.5	6.4	11.2	9.6	7.2	8.8

It can be seen that the dirt content is the most variable factor affecting the yield of the fleece. It is interesting to note that the samples with the highest dirt content are those giving the lowest yield of wool in both merino and crossbred types. These are sample No. 1341, a merino fleece wool from the Bourke District of N.S.W. which contained 43.8 per cent. of red dust and gave an oven-dry wool yield of only 29.4 per cent., and No. 5787, a crossbred sample from the West Wyalong district of N.S.W. which contained 23.7 per cent. of dirt and 49.3 per cent. of oven-dry wool, which is very low for this type of fleece.

Wax after dirt is the constituent having the greatest effect upon the yield. In the cross-bred types, sample No. 5854 has the lowest wax content of 5.3 per cent. and the highest oven-dry yield of 72.2 per cent. .

The suint contents show a variation of about 10 per cent. for both merino and crossbred types.

The least variable of the fleece constituents is the moisture content, the variations of which are much less marked than those of the other constituents. In unusual circumstances, such as when the sheep are shorn wet, the moisture contents can be higher than these recorded.

The maximum and minimum figures given in Table IX refer to *representative* samples of commercial lots of wool. It has been found that small portions chosen from some lots can give figures for fleece constituents outside the above ranges, but these samples are not representative of the lots from which they are drawn. Thus one small sample taken from a bale contained 78 per cent. of dirt in the form of caked mud and only 11.2 per cent. of oven-dry wool, 4.3 per cent. of wax and 0.6 per cent. of suint. Another small sample selected on account of its high wax content was found to contain 40 per cent. of wax. A suint content of 15.0 per cent. was recorded for a small sample of wool from the Kimberley district of W.A. These samples, however, are not representative of any one clip and simply illustrate extreme values of the fleece constituents.

In comparing the different types of fleece wools, it can be seen that the crossbreds contain in general less wax and more suint than the merinos. Furthermore, the merino types usually have higher dirt contents than the crossbred types, probably due to the greater amount of wax in the merino fleece, which facilitates the adherence of dirt. The moisture contents of the crossbred fleeces are in general higher than those of the merino fleeces, which is to be expected as the former contain greater percentages of the two fleece constituents which attract moisture, namely wool and suint. There are no outstanding differences in fleece constitution between the various merino types. Owing to their lower wax and dirt contents, the crossbred types below 58's quality (Table VI) give significantly greater yields of oven-dry wool than those of higher quality (Table V).

Wools fellmongered by soaking in water and then removed from the skins after "sweating" are characterised by extremely low suint contents, as can be seen from an examination of Table VII.

The suint contents in this table have varied from 0.1 to 1.4 per cent., showing that this constituent is removed from the fleece during the soaking process. The dirt contents range from 6.4 to 21.5 per cent., and it seems probable that a certain amount of the dirt is removed in suspension during the fellmongering process. This was investigated by analysing samples taken from fleeces before and after soaking in cold water as in fellmongering. In these experiments a crossbred and merino fleece sample were each immersed in cold water for 24 hours and then removed and squeezed by hand. They were then allowed to dry in the air and analysed. Samples from the original products were also analysed.

Before soaking, the crossbred sample had suint and dirt contents of 10.1 per cent. and 4.4 per cent. respectively. During soaking it was found that 72 per cent. of the original suint and 62 per cent. of the original dirt was removed.

The merino sample had initial suint and dirt contents of 2.7 per cent. and 14.2 per cent. respectively, and of these constituents 72 per cent. of the suint and 22 per cent. of the dirt were removed during soaking. Changes in wax contents were negligible for both crossbred and merino types. It can be seen therefore that dirt as well as suint would be removed during fellmongering.

A considerable amount of data has been obtained concerning the wax and moisture contents of slippe wools. These are in addition to the results set out in Table VII. Of 143 tests for wax content only, it was found that the maximum was 22.3 per cent. and the minimum 11.7 per cent., the average being 14.5 per cent. The average value for moisture was 8.4 per cent. in 98 tests, the range being from 12.3 per cent. to 5.1 per cent.

In Table VIII some results are set out showing the fleece composition of certain samples of black wool. It can be seen that there are no significant differences between the amounts of fleece constituents present in these samples and those of ordinary wool.

SECTION B. SOME PROPERTIES OF THE FLEECE COMPONENTS.

The work in this section was planned to find the scientific basis for views on the properties of the fleece components held by certain wool valuers, and each of the fleece constituents will be discussed separately.

1. Wax.

The opinion is sometimes expressed that the wax in the fleece is attractive to moisture. This is no doubt based upon the fact that lanolin will readily mix with water to form emulsions without the addition of any emulsifying agent. The experiments of Wright (1909) and Hill (1922) also indicate that wool wax can absorb appreciable quantities of moisture from the atmosphere. Conversely, Lennox (1938) showed that the ether-soluble fraction plays a negligible part in the ability of the fleece to absorb moisture from the atmosphere.

Three experiments have been carried out to investigate the above points. Firstly a sample of pure commercial lanolin (3-4 gm.) was weighed and mixed with about one-third of its weight of distilled water to produce a homogeneous emulsion. This was spread thinly on a watch glass, exposed to the atmosphere and protected from dust and the loss in weight due to moisture evaporation determined by daily weighing. The second experiment was undertaken using similar conditions but with the initial addition of 0.1 gm. of powdered suint. In the third experiment a sample of wool wax previously dried and weighed was spread thinly on a watch glass and exposed to the atmosphere with the other two samples, daily weighings being carried out to determine the moisture uptake. In each experiment a small stirring rod was weighed together with the wax, which was thoroughly mixed after each weighing. The experiments were continued for one month, during which room temperature and relative humidity approximated to 75° F. and 50 per cent. respectively without extreme variations.

It was found that the samples to which water had been added lost moisture and came to equilibrium with the atmosphere after a period of 17 days. They then started to *take up* small amounts of moisture. The sample containing suint did not show any increase in its capacity to retain moisture when compared with the sample containing no suint. This was apparently due to the suint being embedded in the wax emulsion and not exposed to the atmosphere. In the fleece, the suint occurs outside the wax layer, and being unprotected from the atmosphere by the latter can markedly exert its hygroscopic properties. The dry wax sample gradually absorbed small amounts of moisture from the atmosphere and appeared to reach equilibrium after 14 days, when the moisture regain was 0.82 per cent. After that there was a slight loss in weight and then a gradual increase. An outline of the results is given in Table X below.

TABLE X.
Moisture Regains of Wool Wax.

Experiment.	Regain* Per Cent.			
	Initial.	After 3 Days.	After 17 Days.	After 31 Days.
(a) Lanolin emulsion ..	30.1	10.9	1.26	1.49
(b) Lanolin emulsion and suint	23.3	9.1	0.67	0.80
(c) Lanolin	0	0.27	0.89	1.44

* The moisture content expressed on the original weight of wax.

These results show that lanolin has no marked ability to attract moisture from the atmosphere. On the contrary, added water tends to dry out on exposure and the equilibrium moisture content is of the order of 1-1½ per cent.

2. Suint.

The most hygroscopic constituent of the fleece is the suint, and when present in unusually high amounts it can exert a marked effect on the total moisture content. Graphs given by

Lennox (*loc. cit.*) show that the moisture regain of suint is of the order of 40 per cent. at 30° C. and a relative humidity of 70 per cent. In the present work, observations have been carried out on two portions of the same lot of greasy wool (No. 5229), one of which was described as "yellow and oily" and the other as "pale and dry". Both portions were analysed as described in Section A of this paper and the following results were obtained:

Sample.	Percentage Composition.				
	Wax.	Suint.	Dirt.	Moisture.	Oven-Dry Wool.
"Oily" portion	13.3	15.0	14.3	13.6	45.2
"Dry" portion	14.8	6.4	17.4	9.4	52.3

These results show that the "oily" portion has considerably higher suint and moisture contents than the "dry" portion. The so-called "oiliness" is no doubt due to the presence of large amounts of highly coloured suint which attracts moisture to that particular portion of the fleece. The excess moisture and the bright yellow colour of the suint bring about the so-called "yellow oily" nature of the fleece. It is of interest to note the suint content of 15 per cent. given above represents 33 per cent. when expressed on the oven-dry weight of wool, which shows that there has been an unusually high secretion of this fleece constituent by the sheep. The wool was a "canary-stained" type from the Kimberley district of Western Australia.

3. Dirt.

It has been shown in Section A that the dirt content of the fleece is one of the most important factors affecting yield. The wool valuer is keenly aware of this and some consider that there are differences in the "weights" of the various types of mineral material picked up by the fleece. Thus "sand" and "grit" are sometimes considered to weigh more than "dust" and "earth" and consequently to have a greater effect on the yield. The view may also be held that the "earthy" dirt contains higher moisture contents than the dusts. To investigate these points we collected various fleece samples which had been described by some practical wool men as "sandy", "gritty", "dusty", etc. Some of the dirt was removed from these samples by opening out the staples by hand and shaking. The moisture content of each dirt sample was determined by drying to constant weight at 100–105° C. and the specific gravity by water displacement in a pycnometer bottle. The results of these experiments are recorded in Table XI.

TABLE XI
Specific Gravity and Moisture Contents of Dirt.

Description of Dirt.	District of Origin.	Moisture Content Per Cent.	Specific Gravity.
Clay-pan dust	Booligal (N.S.W.)	3.0	2.12
Red dust	Wyalong (N.S.W.)	2.7	2.05
Grit	Coonamble (N.S.W.)	3.5	2.01
	North East (S.A.)	2.5	2.33
Yellow, earthy	Far North (S.A.)	2.9	2.39
	Wilcannia (N.S.W.)	2.7	2.31
	Far North (S.A.)	3.3	1.94
	Port Augusta W. (S.A.)	3.1	2.13
Red sand	North West (S.A.)	2.9	2.25
	Upper North (S.A.)	2.3	2.29

These figures show that differences between the specific gravities and moisture contents of the various types of dirt are not substantial. The moisture contents are of the order of 2½–3 per cent., and therefore greater than those recorded for lanolin in the previous experiments of this section. These amounts are not high enough to affect the yield seriously. The differences in

specific gravity although small are actually less than those recorded above as some of the dirt samples contained small amounts of finely divided vegetable material and epithelial debris as well as adsorbed wax,³ which would tend to lower the specific gravity result. These results indicate that for all practical purposes there are no significant differences in specific gravity for the various types of dirt found in the fleece. Differences in "weight" to which the practical man refers are probably differences in the bulkiness and general appearance of the various mineral constituents. The fine dusts tend to spread over the exterior of the fleece and are more noticeable than the coarser sands even though the latter may be present in larger quantities. A similar difference in "bulkiness" has been recorded for vegetable material in an earlier publication (Lipson (1942)).

4. Vegetable Material.

All the wools which have been dealt with in the present paper have contained only small amounts of vegetable material. Other work which has been carried out in this laboratory has shown that the amount of vegetable material in the fleece can at times be quite substantial. In one instance it was as high as 23 per cent. of the fleece weight. It is sometimes maintained that certain types of vegetable material contain substantial amounts of wax or have high moisture contents which considerably affect yields in fleeces containing these types of vegetable material.

These points were investigated by determining the wax and moisture contents of different types of vegetable material hand picked from greasy wool. The wax and moisture percentages were estimated as described earlier for wool. The results are set out in Table XII below, and include as a point of interest data on the relative weights of the different types of vegetable material which were examined.

TABLE XII.

Wax and Moisture Contents and Relative Weights of Vegetable Material. Collected from the Fleece.

Type of Vegetable Material.	Moisture Content Per Cent.	Wax Content Per Cent.	Number of Burrs per Ounce.
Noogoora Burr (<i>A. chinense</i>)	7.4, 7.4, 8.5	0.74, 0.77	95-187
Bathurst Burr (<i>A. spinosum</i>)	7.3	0.50	494-638
Trefoil Clover (<i>M. denticulata</i>) ..	6.7, 7.4	0.71, 0.82	610-725
Small Trefoil (<i>M. minima</i>)	—	—	1440-1985
Shive (<i>Aristida</i> spp.)	13.5	11.6	13,300*

* One estimation only.

No vegetable material taken from greasy wool has shown an excessive moisture content. Only the shive samples had a moisture content above that of the entire fleece, the moisture contents of the fleece samples from which the burrs were taken varying from 8.5 to 10.6 per cent. The wax contents were extremely low except for the shive which had acquired a considerable amount of ether-soluble material from the sheep. This is due to the physical structure of this type of vegetable material (Milthorpe (1943)) which facilitates its movement through the fleece and into the skin of the sheep. The wax had collected mainly at the base of the long narrow "seed" and beneath this wax layer was an accumulation of material which gave a positive test for protein. This latter was no doubt derived from the skin of the sheep, where it had been penetrated by the base of the "seed".

The third column in Table XII, giving the number of burrs per ounce, is significant with regard to the yield of greasy wool. It can be seen that only small numbers of Noogoora and Bathurst burrs need be present in a fleece to affect its yield noticeably, whereas the lighter burrs must be present in substantial numbers before a large effect upon the yield is obtained. Thus if 100 Noogoora burrs (1 oz.) were introduced into 1 lb. of a fleece sample which previously yielded 50.0 per cent. of oven-dry wool, this yield would be reduced to 47.1 per cent. If alternatively

* One sample of dirt contained 4% of ether-soluble material.

100 small Trefoil burrs were introduced into the same sample the oven-dry yield would only be altered to 49·8 per cent.

SUMMARY.

The results of about 200 analyses of different types of Australian fleece wools are reviewed with emphasis on the effect of the various constituents on the yield. The dirt content is found to be the most variable factor affecting the yield, its range being 6·3–43·8 per cent. for merino fleece wools and 4·3–23·7 per cent. for cross-bred wools. The least variable of the fleece constituents was the moisture content, being 8·1–12·6 per cent. for merinos and 9·5–14·2 per cent. for cross-breds.

The cross-bred fleeces have in general higher suint and lower wax contents than the merinos.

Wools which have been fellmongered by soaking and “sweating” are characterized by low suint and reduced dirt contents.

Experiments were carried out to examine views which have occasionally been propounded concerning properties of the individual fleece components.

It was found that lanolin has no marked capacity to absorb atmospheric moisture, and when mixed with water will dry out in the atmosphere to an equilibrium moisture content of 1–1½ per cent.

The moisture content of the dirt in the fleece is of the order of 2½–3 per cent.

There are no large differences in specific gravity for the different types of dirt. Suint is the most hygroscopic fleece component, and when present in large amounts can attract considerable quantities of moisture to give rise to a condition in the fleece known as “oily”. A fleece sample of the latter description was found to contain 15·0 per cent. of suint and to have a moisture content of 13·6 per cent. Vegetable material collected from fleece samples had moisture contents ranging from 7·3 per cent. to 13·5 per cent. The vegetable material contained little ether-soluble matter except for “Shive” (*Aristida* spp.), which had picked up considerable quantities of wax in penetrating the skin of the sheep.

When vegetable material is present in the fleece the effect on the yield varies considerably with the type of vegetable matter owing to differences in the relative weights of various burrs.

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THE BAUXITES OF NEW SOUTH WALES.

THEIR DISTRIBUTION, COMPOSITION AND PROBABLE ORIGIN.

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With Plates II-III and two Text-figures.

(Presented by permission of the Under Secretary for Mines.)

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INTRODUCTION.

The terms laterite and bauxite have been used in the past to describe a variety of different materials. Definitions of these terms, as adopted by the writer, are given at this stage in order to make the paper more easily understandable, even at the risk of anticipating somewhat the section on origin. The term laterite, which is the more inclusive, is taken to embrace all material which has been formed by the weathering of suitable rocks in such a way as to remove in solution from at least one layer in the weathered profile the bulk of silica, lime, magnesia, potash, soda, etc., leaving an accumulation relatively rich in hydrated oxides of iron and aluminium. Varieties in which the iron oxide content exceeds or is about equal to that of the alumina are simply referred to as laterite, while those containing large proportions of alumina, silica or titania are distinguished by the adjectives aluminous, siliceous and titaniferous respectively. Constant usage in industry of the term bauxite has led to it being applied to material, consisting mainly of oxides of aluminium, which is suitable for use as an ore of that metal. This meaning is used throughout the following, with the adjectives ferruginous and siliceous qualifying varieties which contain considerable percentages of iron oxide and silica respectively. The terminology adopted leads to a certain amount of duplication, but this is difficult to avoid. Aluminous laterites, low in silica, could be regarded as bauxites, but this should not be taken to imply that all bauxites are necessarily of lateritic origin.

It should be stated that the writer considers that all lateritic deposits are primarily the products of weathering *in situ*. Once formed, the laterites may be redistributed by the agency of running water and laid down as a sedimentary formation. Deposits which may have been laid down under water as the results of interaction between solutions containing suitable chemicals would not be regarded as laterites.

The information on which this paper is based was obtained during field-work in company with Dr. H. G. Raggatt in the Bundanoon-Wingello district and Mr. F. W. Booker, M.Sc., in the Tingha-Inverell-Emmaville district. It deals mainly with deposits of material which could be regarded as potential ores of aluminium, and has therefore been entitled "The Bauxites of New South Wales". Other lateritic deposits, which are either too low in alumina or too high in silica to be regarded as potential ores of aluminium, are only discussed incidentally. The Bungonia-Windellama deposits are too low grade to be regarded as potential ores of aluminium unless they are found to be amenable to beneficiation. They have been dealt with in this paper because of their close association with the Bundanoon-Wingello deposits, of which they may be regarded as being a south-westerly extension.

The first record of the occurrence in New South Wales of lateritic material was made by Wilkinson in 1875. Certain aspects of its occurrence were discussed by David (1887) and Carne (1911). More comprehensive reports, particularly in regard to the Wingello deposits, were made by Jaquet (1899, 1901). Later Harper (1924) made a reconnaissance examination of the bauxite deposits of the State. Just prior to the outbreak of the present war, it was decided to assess the State's resources of potential aluminium ore. Departmental reports were made by Raggatt (1939) on the Bundanoon-Wingello deposits; Mulholland (1941) on Trundle, Crookwell and Bungonia-Windellama deposits, and Booker and Hanlon (1944) on the Tingha-Inverell-Emmaville deposits. The information contained in these reports has been freely used in the compilation of this paper. The views expressed throughout the paper are, however, except where acknowledged, entirely those of the writer.

The analyses quoted, except where otherwise stated, were all carried out in the Departmental Laboratory. The writer wishes to thank sincerely Dr. W. R. Browne for many helpful suggestions, Mr. W. Curteis for information gained in discussions, particularly relative to the Victorian deposits, and Mr. H. F. Whitworth, M.Sc., who took the photographs of the micro-sections accompanying this paper.

GEOGRAPHY.

The distribution of the bauxite and associated deposits throughout the State is shown on the accompanying locality map, Figure 1, which also conveys some idea of the disposition with regard to rail transport. All deposits are easily accessible by road. The spots are only intended to show the approximate location of each group of deposits.

With the exception of the Trundle area the deposits are situated on an irregular plateau, at elevations varying from about 2,000 feet A.S.L. to slightly over 3,000 feet A.S.L. The principal deposits in the Tingha-Inverell-Emmaville district (Booker and Hanlon, 1944), which are situated on portion of the New England Plateau, have basal heights varying from 2,340 feet for one deposit nine miles west of Inverell to 3,080 feet for one at Emmaville. Some unsurveyed deposits further to the east are still higher. The Bundanoon-Wingello deposits (Raggatt, 1939) are situated on the northern part of the Southern Tableland at heights varying from 2,180 feet to 2,426 feet. The Bungonia-Windellama deposits (Mulholland, 1941) may be regarded as a south-westerly extension of the Bundanoon-Wingello deposits. They occur as cappings to a number of mesa-like hills at 2,010 feet to 2,050 feet A.S.L. The Crookwell deposits lie at an elevation of about 3,000 feet. At Trundle the type of occurrence differs somewhat, the deposits being only about 850 feet A.S.L. In all cases the deposits form part of the present land surface and are not overlain by either sediments or volcanic rocks.

The physiography at the time of the formation of the bauxites is discussed below.

GENERAL GEOLOGY.

The bauxites of New South Wales are, with the exception of those at Trundle, associated with Tertiary volcanic rocks. These bauxites form only one group of the laterites of New South Wales. Other lateritic deposits are widespread and have been formed from a variety of different rocks. At French's Forest, near Sydney, and in other parts of Sydney district, they have been formed on Mesozoic clays or clay shales and possibly in some instances on argillaceous sandstone. A large portion of western New South Wales has a surface crust of "grey billy", which has probably been formed, like the laterites, as a layer in the soil profile during weathering. In most areas of the State, where remnants of

J—September 6, 1944.

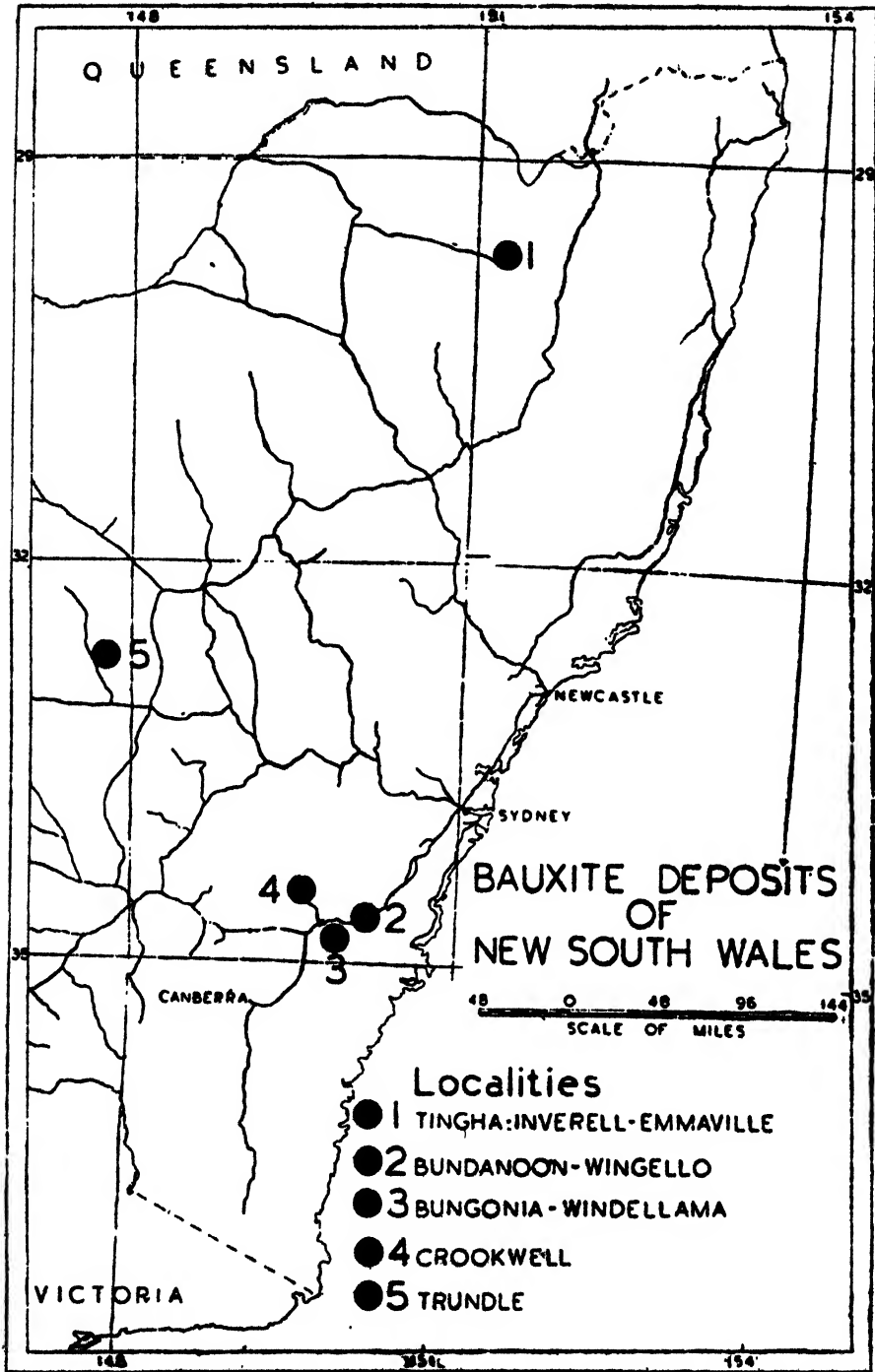


Fig. I.—Bauxite deposits of New South Wales.

the Tertiary peneplain are preserved, there are some points at which deposits of lateritic or similar origin can be found.

The basement rocks underlying the Tertiary volcanic rocks at points where the bauxites occur vary with the district. At Tingha-Inverell-Emmaville they consist of claystones, tuffs and lavas of Permian (Lower Marine) age, which have been extensively intruded by granite. At Crookwell they are Silurian sediments which also have been intruded by granite. The Bundanoon-Wingello and Bungonia-Windellama deposits overlie Tertiary sediments. These sediments at the former locality, in turn overlie Mesozoic sediments. The Trundle bauxites are considered to be derived from a mauve-coloured felspathic rock which is probably a tuff. Mulholland (1941) considers these tuffs to be of Devonian age or younger, probably Mesozoic. Booker (1941) alternatively considers the parent rock to be andesite or andesitic tuff of Upper Silurian age.

The basalts with which the bauxites are associated are probably of Oligocene age. From the evidence of foraminifera (Crespin, 1943) occurring in the clays interbedded with the lignites overlying the lateritised volcanic rocks, Dr. G. H. Raggatt (private communication) considers that the bauxites of Gippsland in Victoria are either Lower Miocene or Lower Middle Miocene. Bryan (1938) is of the opinion that the red-earths of south-eastern Queensland were formed during Pliocene time. Whitehouse (1940) considers that there were two periods of lateritisation in Queensland, both in the Pliocene, which were separated by a period of aridity. In New South Wales there is no direct evidence of any of the deposits having ever been covered by later sediments as in Victoria. The writer considers that the periods of lateritisation in these two States were probably coincident, corresponding with Woolnough's (1927) Australian-wide formation of duricrust in Miocene time. Lateritisation may have continued further into the Miocene period in this State than in Victoria, unless the period of sedimentation there was accompanied by such general changes in climate as to render further lateritisation impossible. There may have been two periods of lateritisation here as suggested for Queensland, although the writer has seen no evidence to support it. Andrews (1910) has pointed out that the Tertiary flora of eastern Australia was uniform and evidenced a mild to tropical climate.

There is no direct evidence of two ages of basalt in any of the areas examined. The fact that basalt occurs at different levels cannot be taken as irrefutable evidence for two ages of basalt, because in places, for example about 10 miles from Inverell on the road to Copeton (see Plate II) the basalt can be seen passing uninterruptedly from the higher ground, over the granite basement and down into the valley of the MacIntyre River.

The present distribution of the bauxite deposits is related to the physiography, in Tertiary time, of the districts under consideration and also to the previous extent of the basalts and the amount of erosion to which they have been subjected since their consolidation. There seem to be indications that the relief of the New England Plateau and northern part of the Southern Tableland in Tertiary time immediately prior to the period of vulcanicity was comparable with that of the present day, although perhaps not so marked. Voisey (1942) has demonstrated inequalities of the pre-basalt surface of over 1,400 feet for the southern portion of the New England. Differences of over 200 feet have been recorded by Booker (1938) at Cherry Tree Hill. The photograph in Plate II taken from the lookout above Inverell, shows surface relief amounting to at least a few hundred feet. Andrews (1903, 1904) records considerable differences in elevation of the basement rocks underlying the basalts. Although little evidence has been collected, the general impression is gained that the relief of the pre-basalt surface in the Bundanoon-Wingello area was less than in the New England district.

It would be fallacious to argue that great thicknesses of basalt must have covered low lying ground, simply because similar thicknesses covered ground at points in adjacent areas. Some basalt flows from fissure eruptions in Iceland have a surface slope of just slightly more than half a degree (Cleland, 1916). These flows were extremely fluid and would probably approximate to the limiting value for the slope of the upper surface of basalt flows. Raggatt (1939) records that the upper surface of the bauxite deposits (and hence of the former basalt surface immediately preceding lateritisation.—F.N.H.) in the Bundanoon-Wingello district, shows a steady fall from north to south of approximately 30 feet to the mile. This slope has probably been affected by post-basalt tilting. The greatest thickness of basalt measured in the New England area approximates 1,500 feet and occurs in the Guy Fawkes district (Andrews, 1903). Assuming a level basement, a slope of the upper surface of a basalt flow of only half a degree (equivalent to approximately 46 feet in a mile) would account for the complete thinning out of a flow of that thickness in less than 33 miles.

The writer believes that the amount of post-lateritisation erosion in the areas in which the bauxites occur has been small. In support of this contention the evidence from the locality of Inverell is quoted. The bed of the MacIntyre River in that vicinity is occupied by basalt, as also is the higher ground to the west. The present drainage flows easterly from these hills to the MacIntyre. Had the surface level of the basalt been higher at Inverell than to the west, it is hardly conceivable that the main drainage of the district would have established itself at Inverell. The present elevation of the MacIntyre River at Inverell is about 1,900 feet A.S.L., while at a bauxite deposit four miles west of the town the surface elevation is 2,530 feet A.S.L. As only the surface layer of the basalt could be lateritised, the bauxite must represent approximately the pre-lateritisation surface of the basalt. Assuming that the basalt reached the same level above Inverell as at the Four-Mile deposit, the thickness of the basalt eroded from the valley of the MacIntyre since the completion of lateritisation in that area could not have exceeded 630 feet. In the vicinity of the Four-Mile bauxite deposit, the erosion of basalt since the lateritisation of its surface must have been negligible, or otherwise the bauxite would have been removed. This gives a range for the amount of basalt eroded in the Inverell district of from practically nil in the vicinity of the laterite or bauxite deposits to a maximum of 630 feet in the valley of the MacIntyre. This is not necessarily the total amount of erosion since the eruption of the basalts because no account has been taken of any sediments or younger volcanic rocks, which may have subsequently covered the basalts and since been entirely removed by erosion, nor of any contemporaneous inter-flow erosion, nor of erosion subsequent to the eruption of the basalts but prior to their lateritisation. There is evidence of some contemporaneous inter-flow erosion and sedimentation in river valleys in both New South Wales and Victoria. However, the writer has not seen any definite evidence of younger rocks covering the basalts in the neighbourhood of the New South Wales bauxites.

The extremely slow rate of erosion in the neighbourhood of the laterite deposits is probably explained by the protection afforded by the surrounding region which slopes gently away from them. The lateritic capping may also have increased the resistance to erosion at points where it occurred. Easterly from the Four-Mile deposit the average slope for the first two or three miles is quite gentle and it is only within a mile or so of Inverell that the slope down the side of the MacIntyre Valley becomes appreciable. Lateritisation was certainly much more widespread than present areas indicate, but areas of laterite not protected by surrounding regions of gentle slope have probably been removed by erosion.

The general low rate of erosion in areas occupied by the bauxite deposits of the Tingha-Inverell-Emmaville area can probably be explained by the relatively gentle slope to the west and the protection afforded against active coastal streams to the east by the higher ground of the main part of the New England Plateau. On the eastern fall of the plateau there is abundant evidence of active erosion since Miocene time. This probably accounts for the relative paucity of lateritic deposits in that area.

During Oligocene time immediately prior to the eruption of the basalts, the land surface was probably an old peneplain which had been moderately uplifted and subsequently suffered erosion to produce valleys several hundred feet in depth. Isolated peaks, rising above the peneplain surface, were some 2,000 feet A.S.L. Following the eruption of the basalt, during which some readjustments in elevation took place, there was vertical uplift during the late Miocene and late Pliocene (Andrews, 1903, 1927). This uplift would have become progressively less proceeding westwards from the main divide, and, except for readjustments accompanying recent movements in the coastal areas, would have resulted in elevating the area approximately to its present position.

The relationship of the Trundle bauxite to the other deposits now becomes clearer. The lateritisation over the areas under consideration took place during Miocene time, when the elevation of the land surface was between sea level and not much over 2,000 feet, the greater portion of it being considerably lower than the latter figure. Lateritisation in these areas was probably widespread where rocks of suitable composition outcropped. In the New England and Southern Tableland districts they consisted of basalts, while further to the west at Trundle, an area not affected by Tertiary volcanic eruptions, tuffs belonging to an earlier period became lateritised. While the bauxites of the districts nearer the coast were uplifted to over 2,000 feet during Pliocene time, those at Trundle suffered very little change and their present height is only about 850 feet A.S.L.

COMPOSITION OF NEW SOUTH WALES DEPOSITS.

Although some high grade bauxites have been found in New South Wales, the bulk of the deposits should more aptly be referred to as ferruginous bauxites. The average composition of many millions of tons of material from the Tingha-Inverell-Emmaville district is shown in Table I.

TABLE I.
*Average Composition of the Ferruginous Bauxites from
Tingha-Inverell-Emmaville.*

Constituent.	Average Composition.
Alumina	39.5
Silica	4.5
Ferric oxide	30.0
Titania	4.0
Loss on ignition	22.0
Ratio of alumina to ferric oxide ..	1.3

The Bundanoon-Wingello deposits are very similar in composition to the above, except that the alumina percentage is slightly lower and the ferric oxide slightly higher in most of the deposits. Their south-westerly extension, the

Bungonia-Windellama deposits, are very siliceous. The Crookwell deposits are similar to those at Bundanoon-Wingello. The Trundle deposits are generally lower in grade than these, although small quantities have been found which contain 60% alumina. A fair tonnage from one deposit at Sutton Forest in the Bundanoon-Wingello district contains about 52% alumina, while samples have been obtained from the Four-Mile deposit near Inverell which contain over 50% alumina.

The bauxitic material mostly has a characteristic reddish-brown colour, but both colour and texture are variable. The high grade material, referred to above, from Sutton Forest, is earthy and almost white in colour. The most characteristic texture is pisolitic, but vermicular, lithoidal, earthy, nodular and concretionary types are common. The pisolites vary from microscopic dimensions to more than an inch in diameter, the commonest size having a diameter of about a quarter of an inch.

Magnetic concentration tests were carried out by Mr. H. F. Whitworth, Curator of the Mining Museum, on a sample of pisolitic bauxite. The pisolites were fairly uniform in size, averaging about three-sixteenths of an inch in diameter. Their separation into three fractions was made by means of an ordinary horseshoe magnet. Those which could be picked up by the magnet were classified as magnetic, those which could be moved but not picked up by the magnet as feebly magnetic and the remainder not visibly affected by the magnet as non-magnetic. Some of the matrix in which the pisolites were embedded was also separated from the original sample. The percentages of alumina extracted from the samples by a hot 10% solution of sodium hydroxide are shown in Table II. The alumina extracted by this method is referred to as "free" alumina.

TABLE II.
*Results of Magnetic Concentration Tests of Pisolithic
Ferruginous Bauxites.*

Product.	"Free" Alumina.
Bauxite (original)	33.3%
Matrix	39.4%
Magnetic pisolites	4.2%
Feebly magnetic pisolites	20.8%
Non-magnetic pisolites	27.2%

The vermicular material contains tubular openings up to three-quarters of an inch in diameter and is commonly mottled, the lighter coloured portion mostly being associated with the tubular openings (see Plate II). An analysis of one sample of the lighter coloured material showed 55.6% alumina and 4.5% ferric oxide, as against 51.3% alumina and 8.5% ferric oxide for the bulk sample. The best concretionary material comes from Trundle. Some of the concretions from this district contain up to 60% alumina and are either loosely cemented together or lying loose in thin beds with the interstices around the concretions filled with red loam. At the Four-Mile deposit, near Inverell, the bauxite occurs in a nodular form, containing up to 50% alumina (see Table 5), the internodular material being reddish-brown and earthy with an alumina content of about 30% (see Plate III).

Before dealing with the mineralogical composition of the bauxites it is helpful to consider the parent rocks from which they have been derived. There

is definite evidence in many cases that these are basalts. Sections have been cut of the bauxites from the Four-Mile (see Plate II for micro-photograph and Table V for analysis), Bundarra Road and Lorne deposits, in which the "basaltic" structure is plainly visible. The original felspar laths now consist of aggregates of gibbsite crystals. In the case of the Four-Mile deposit this structure is seen in the nodular bauxite. Since these nodules make up the bulk of the deposit, as can be seen in Plate III, it is evident that the deposit, as a whole, has been derived by the alteration of basalt. At the Bundarra Road and Lorne deposits, bauxites with pisolitic, vermicular and "basaltic" structures are associated. These overlie kaolinised basalts (see Plate II); which in turn overlie fresh basalts. In many other instances the pisolitic and vermicular bauxites overlie kaolinised and fresh basalts, indicating that they too were derived from basalts. The derivation of some of the Bundanoon-Wingello bauxites from basalt has been traced by Whitworth (1939). When the bauxites directly overlie Tertiary sediments, it is considered that they have been derived from remnants of basalt which previously covered the sediments and have been completely altered to bauxite.

The basalts contain all the constituents necessary for the formation of the bauxites. The analyses of two samples from near Inverell are shown in Table III.

TABLE III.

Analyses of Basalts from Inverell.

Constituent.	Byron, Inverell.	Rob Roy Gully, Inverell.
SiO ₂	44.70	50.54
Al ₂ O ₃	17.28	12.77
Fe ₂ O ₃	2.10	2.50
FeO	9.63	8.01
MgO	8.24	5.89
CaO	9.24	9.24
Na ₂ O	2.28	3.33
K ₂ O	1.31	0.57
H ₂ O at 100° C.	1.21	1.24
H ₂ O at 100° C. +	2.83	1.96
CO ₂	0.14	2.07
TiO ₂	0.56	1.80
ZrO ₂	0.08	absent
P ₂ O ₅	0.45	0.23
SO ₂	Absent	Absent
Cl	Trace	Absent
S (as FeS ₂)	Absent	Absent
Cr ₂ O ₃	0.02	0.01
NiO, CoO	0.02	Absent
MnO	0.10	0.11
BaO	0.02	Absent
SrO	Trace	Trace
Li ₂ O	Absent	Absent
V ₂ O ₅	0.01	0.04
	100.22	100.31
Specific gravity	2.876	2.808

It is interesting to note that the alumina : ferric oxide ratios (the total iron content of the rock calculated as ferric oxide) in these rocks correspond with the

average of the bauxites. The alumina : ferric oxide ratios of a series of New South Wales Tertiary basalts are given in Table IV.

TABLE IV.

Alumina : Ferric Oxide Ratios of Basalts from New South Wales.

Rock.	Locality.	Ratio of Alumina to Ferric Oxide.*
Olivine basalt	Byron, Inverell	1.35
" "	Rob Roy Gully, Inverell	1.12
" "	Tweed River Heads	1.12
" "	Canoblas Mountains, Orange	1.21
" "	Mount Apsley, Bathurst	1.41
" "	Black Head, Ballina	1.33
" "	Gulgong	1.61
" "	Mount Tomah	1.45
" "	Camden Park	1.23
" "	Seal Bay	1.12
" "	Hurstville	1.03
" "	Rookwood	1.28
" "	Dundas Quarry	1.50
Dolerite	Guilford	1.19
"	Long Reef, Narrabeen	1.31
"	Prospect Quarry	1.18
Analcite basalt	Bondi	1.26
" "	Bondi	1.24
" "	Fernhill, Canterbury	1.07
" "	Luddenham	1.22
Leucite basalt	El Capitan	0.71
" "	Byrock	0.86

* Total iron content of the rock calculated as ferric oxide.

The ratios for about 120 bauxites from the Tingha-Inverell-Emmaville district, for which complete shaft sections are available, gave only one value below the lowest and only nine values above the highest of those in Table IV. This indicates that, in most of the deposits, there has been very little relative movement between the alumina and ferric oxide and that the lateritisation has consisted essentially in the removal of silica, lime, alkalis, etc.

The alumina of the bauxites is derived mainly from the plagioclase, to a smaller extent from feldspathoids, such as nepheline and leucite, and also from analcite and the ferro-magnesian minerals. In many of the basalts the augite is a purple titaniferous variety and supplies part of both the iron and titanium. Olivine phenocrysts are abundant as also are small grains of magnetite and ilmenite. Petrological descriptions of Tertiary basalts from New South Wales have been given by Card (1903), Browne (1933) and Whitworth (1939).

The present mineral constitution of the bauxites is difficult to determine in the absence of X-ray examinations. Micro-slides were made of many samples, but in most cases the constituents show no crystal structure, appear quite amorphous and are indeterminate.

Chemical analyses and the study of micro-sections indicate that the silica is present mostly in the combined form in various clay minerals, although none of these was definitely identified. Free silica was identified only as grains of quartz in samples from the Bundanoon-Wingello district. In this connection Whitworth (1939) states, "A number of waterworn grains of quartz are present in the laterite; these obviously have not been derived from the basalt and imply

that, at some stage in the alteration from basalt to laterite, cracks of some size have formed and allowed sand grains to be washed or blown in and that subsequently the cracks have been sealed by iron and aluminium oxides or hydroxides. In some places later cracks have parted both the laterite and included quartz grains, and iron oxide cement may be seen traversing grains of quartz." In cases where the bauxite has been derived from only a thin layer of basalt resting on Tertiary sandstones the full thickness of the basalt has been altered and the underlying sandstones affected also. In some instances when the basalt was flowing over the sandstone, fragments may have been caught up in the lower levels of the basalt. Lateritisation of such material would lead to an intimate mixing of the lateritic constituents with quartz grains. In some of the deposits the surface layers are relatively rich in silica and it is possible that some of this may have been redeposited in a free hydrated colloidal form.

The results of chemical analyses indicate that the alumina occurs in the free hydrated form except for that portion which is combined with the silica. A sample obtained from the base of one deposit in the Wingello district was considered by Mr. H. F. Whitworth (1939) to be crude emery. The corundum which occurred in this sample was, however, probably present as such in the basalt and was not a product of weathering. Primary segregations of emery in basalts from New South Wales are quite common, deposits having been prospected at Inverell, Quirindi and Crookwell. The only hydrated form of alumina which has been positively identified in any of the slides is the alpha-trihydrate, gibbsite. For those samples in which the gibbsite can be recognised, the analyses show sufficient water to combine with the alumina present as the trihydrate. A section from one of the Trundle concretions consists of a finely crystalline aggregate of what is probably gibbsite. The constituents in the pisolitic forms are mostly unidentifiable, but where gibbsite can be recognised it occurs interstitially or in cracks crossing the pisolites. The constituents of the earthy and vermicular types are unidentifiable in any sections made. Rogers and Kerr (1942) have given the name cliachite ($\text{Al}_2\text{O}_3 \cdot (\text{H}_2\text{O})_x$) to the amorphous forms of hydrated alumina occurring in bauxites. Most analyses, of no matter what type of bauxite, show a sufficient water content to satisfy the alumina present in the form of the trihydrate. In some samples, however, the water content is insufficient to satisfy this form, so that portion at least must occur in some less hydrated form, either as the alpha-monohydrate (boehmite), the beta-monohydrate (diaspore) or some colloidal form. This conclusion is strengthened by the fact that where the water present is insufficient to form gibbsite with all the alumina, the analyses always show an increase in the difference between the total alumina and that soluble in caustic soda solution. Neither boehmite nor diaspore was, however, recognised microscopically in any of the samples examined. Many investigators consider that the alumina, and also the iron and silica, are present in a colloidal form as uncombined oxides or hydrogels. Taking all the evidence into consideration, the most likely assumption is that in the New South Wales bauxites most of the alumina occurs as gibbsite. In some cases, subordinate amounts might occur as boehmite or diaspore with possibly colloidal compounds of variable hydration. Alternatively the alumina in the bauxites might possibly be considered as occurring mainly as the mineraloid cliachite, with subordinate amounts in the crystalline form as gibbsite.

Magnetite and ilmenite are abundant in the basalts, and magnetite and hematite have both been observed in samples of the bauxites. Mostly, however, the iron occurs in a quite unidentifiable form and varies from yellowish to reddish-brown in colour. The fact that some of the pisolites are easily picked up by a horse-shoe magnet, points to portion of their iron content occurring as magnetite. The likelihood of the occurrence of ilmenite is dealt with below in

connection with the titanium minerals. According to Raggatt (1939), the magnetic properties of the bauxites suggest that the iron occurs mainly as hematite. Provided that in some cases the alumina is assumed to occur largely as a monohydrate, there is always enough water present to provide a sufficient degree of hydration to form, at least, turgite. However, as it seems doubtful in many cases whether large proportions of the monohydrate of alumina occur, at least part of the iron must occur as hematite. Where there is a surplus of water present after satisfying the hydration of the alumina and titania (see below), hydrated oxides of iron could exist and might occur either in cryptocrystalline form or as colloids.

The form in which the titanium occurs is doubtful. One sample from Sutton Forest, which was given to the writer by Mr. W. Curteis, contained 10% titania. Ilmenite has been recorded as a constituent of bauxites, and it seems possible that part, at least, of any ferrous iron present in the New South Wales deposits may occur in this mineral, having survived unaltered during the process of lateritisation. Mostly, however, there is insufficient ferrous iron present in the New South Wales bauxites to satisfy all the titania as ilmenite, so that part, at least, of the titania must occur in some other form. Most investigators consider the titanium in bauxites occurs in a colloidal form as either meta- or ortho-titanic acid. Several have suggested xanthitane as a possible constituent.

The analyses of a series of samples taken from a quarry between Stannifer and Tingha (see Plate III) are shown in Table V. The first three samples were taken from the quarry face and the others from a shaft in the floor of the quarry. All depths, including those in the shaft, are expressed from the ground surface at the top of the quarry. This series was chosen because it shows a variation of the different constituents and the sampling has been continued below the limits of lateritisation, although the basalt in the bottom of the shaft is decomposed. The alumina : ferric oxide ratios are also shown.

TABLE V.

Analyses of Bauxites from Stannifer and Inverell.

Location.	Alumina.	Silica.	Ferrous Oxide.	Ferric Oxide.	Titania.	Loss on Ignition.	Hygroscopic Moisture.	Alumina: Ferric Oxide.*
<i>Stannifer Deposit.</i>								
Quarry face—								
0-5' ..	38.5	9.8	2.8	30.9	2.5	12.3	2.0	1.13
5-10' ..	40.6	4.8	2.3	32.0	2.7	14.6	2.0	1.17
10-12' ..	38.3	4.2	0.9	32.0	3.3	17.7	2.1	1.16
Shaft—								
12-17' ..	43.4	3.4	1.4	30.2	2.1	16.2	1.9	1.36
17-22' ..	38.2	4.4	1.0	30.8	3.3	20.3	1.9	1.20
22-27' ..	27.7	28.1	—	26.0	2.8	12.2	2.2	1.07
27-32' ..	28.0	28.6	0.5	24.2	3.4	13.0	2.3	1.13
32-37' ..	28.4	29.5	0.6	22.7	3.3	13.1	2.0	1.21
<i>Four-Mile Deposit.</i>								
North side ..	48.4	2.7	0.4	17.4	3.6	26.3	1.3	2.70
South side ..	50.5	2.0	0.4	15.5	2.1	28.2	0.9	3.15

* The total iron content calculated as ferric oxide.

Possible compositions corresponding to the analyses in Table V are shown in Table VI. In calculating these compositions it was not considered likely that there would be a greater percentage of combined silica at the surface than lower down. For this reason the amount of silica in the sample containing the least of this constituent has been taken as the maximum amount occurring in the combined form in the upper levels of the deposit. Silica in excess of this amount has been shown as free silica without stating the form in which it might occur. The combined silica has been shown as kaolinite, which is considered the most likely mineral in which it might occur. Below the level of the sample containing the least silica, all of this constituent has been shown in the combined form as kaolinite. The titania has been distributed partly as meta-titanic acid and partly as ilmenite. It is not considered likely that the clay at the base would contain more meta-titanic acid than the laterite above, since chemical action would have been more intense closer to the surface. For this reason, only the titania in excess of that required to form the amount of meta-titanic acid in the clay has been expressed as ilmenite. Any ferrous iron not combined with titania to form ilmenite has been shown as combined with ferric oxide and expressed as magnetite. The alumina where the water content was sufficient has been shown as gibbsite; where insufficient, as a mixture of gibbsite and diaspore or boehmite. Where the water is more than sufficient to satisfy all the alumina as gibbsite, the surplus has been shown as combined with iron in the proportions necessary to form limonite. Any iron remaining has been expressed as hematite. The mineral compositions shown in this table are not intended to convey the impression that they are necessarily the actual percentage mineral compositions, especially because no account has been taken of any possible colloidal constituents other than meta-titanic acid. The table has been included in order to aid the appreciation of the variation in both the degree of hydration and the possible forms of chemical combination of the various constituents at different depths.

One of the most noteworthy features disclosed by Table VI is the parallelism of the degree of hydration of the aluminium and iron-bearing constituents in the Stannifer deposit. In samples where there is insufficient water to form gibbsite with all the alumina there is a surplus of ferrous iron to form magnetite.

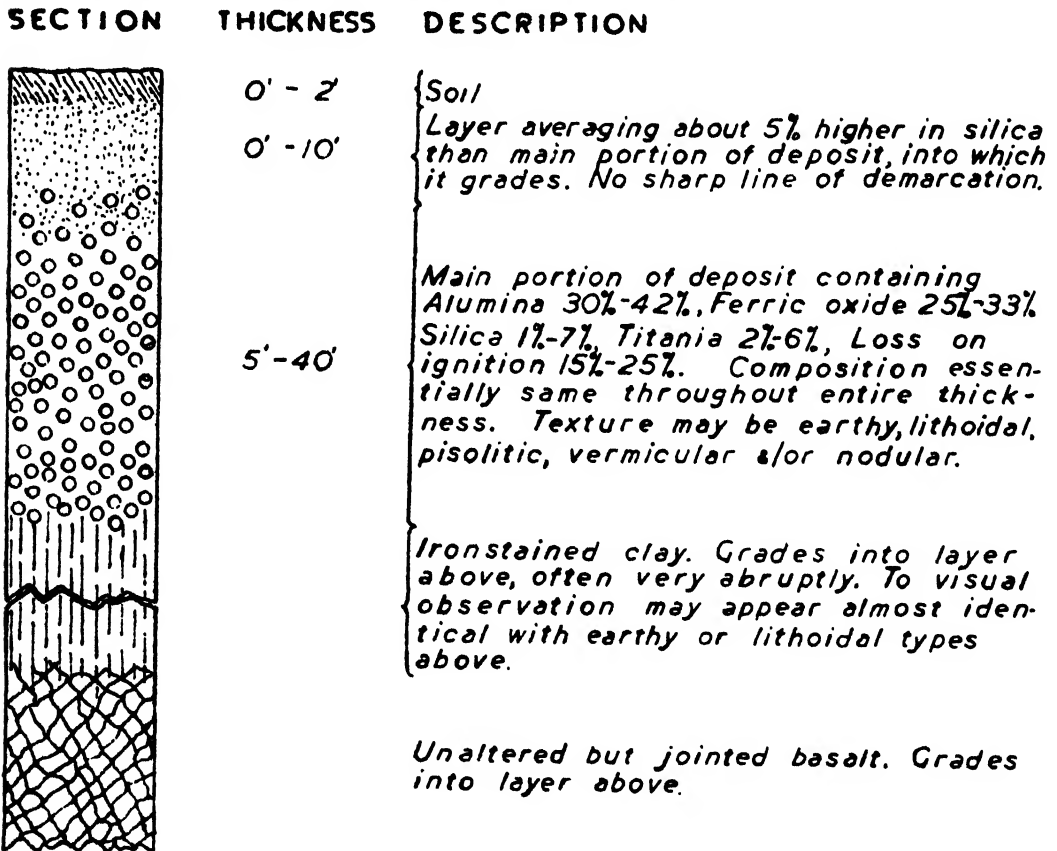
TABLE VI.

Calculated Possible Compositions of Samples shown in Table V.

Location.	Free Silica.	Kaolinite.	Ilmenite.	Meta-Titanic Acid.	Gibbsite.	Boehmite Diaspore.	Limonite.	Hematite.	Magnetite.
<i>Stannifer Deposit.</i>									
Quarry face—									
0-5' ..	6.6	7.6	—	3.2	19.4	28.3	—	25.6	9.3
5-10' ..	1.5	7.6	—	3.4	27.7	24.4	—	27.8	7.6
10-12' ..	0.8	7.6	1.0	3.5	44.1	8.7	—	32.1	1.5
Shaft—									
12-17' ..	—	7.6	—	2.7	33.4	23.6	—	28.0	4.7
17-22' ..	—	9.6	1.0	3.5	53.9	—	0.4	30.0	1.6
22-27' ..	—	62.5	—	3.5	5.9	—	4.7	23.4	—
27-32' ..	—	62.9	1.1	3.5	5.9	—	7.4	19.2	—
32-37' ..	—	65.1	1.3	3.3	5.1	—	7.8	17.4	—
<i>Four-Mile Deposit.</i>									
North side ..	—	5.9	0.9	2.7	72.5	—	0.8	17.2	—
South side ..	—	4.4	0.9	2.0	75.5	—	5.7	11.5	—

The calculated percentage of magnetite present in any sample roughly parallels the calculated percentage of boehmite or diaspore. The variation in the degree of hydration of the material with depth can probably be best explained by the action of atmospheric agencies subsequent to the formation of the deposit, particularly to the heating action of the sun's rays. The samples from the quarry face probably represent fairly closely the original condition of the deposit before quarrying operations. Some dehydration has probably taken place due to exposure, but the aspect of the face sampled is such that it is protected from the action of the sun's rays for the greater part of the day. On the other hand the floor of the quarry receives the full effect of the midday sun. This is probably the cause of the greater degree of dehydration of the sample from the top of the shaft in the quarry floor as compared with the sample from the base of the quarry. Other important features are the concentration of silica in the surface layers of the deposit and the abrupt change to clay at a depth of 22 feet.

The variations shown are not typical of all the deposits. Considering now the examination of nearly 600 samples taken from various shafts of the New South



DIAGRAMMATIC SECTION OF TYPICAL FERRUGINOUS BAUXITES DERIVED FROM BASALT

Fig. 2.—Diagrammatic section of ferruginous bauxite deposit derived from basalt.

Wales deposits, it is found that in most instances average grade bauxite occurs within a few feet of the surface and continues practically unchanged for some depth. The maximum depth measured for any deposit was over 43 feet on Graveyard Creek Lead at Emmaville. At the bottom of each deposit there is generally an abrupt rise in the silica percentage. In many cases there is a concentration of silica in the surface layers. The degree of hydration is variable within certain limits, mostly increasing with depth, but in many cases remaining fairly constant or showing haphazard variation. The alumina: ferric oxide ratios sometimes increase with depth, in many cases remain fairly constant, and at other times decrease with depth. Where the alumina-ignition loss ratio is relatively high, the alumina soluble in caustic soda solution is correspondingly low. A diagrammatic section illustrating the general features of the ferruginous bauxite deposits (except those at Trundle) is given in Fig. 2.

All the layers indicated are not present in every deposit. In some cases either or both of the soil and high silica layers are absent. Sometimes the deposit is not underlain by fresh basalt but directly overlies Tertiary clays or sandstones, the upper portions of which have been altered during the lateritisation of the overlying material.

ORIGIN OF NEW SOUTH WALES BAUXITES.

The New South Wales deposits are not being formed at present, but are in the nature of "fossil" bauxites, having originated during the Miocene period.

When the analyses of the rocks referred to in Table IV are examined, it is seen that the aluminium, iron and titanium oxides constitute approximately 25% of the constituents. If allowance be made for about 4.5% silica and 22% loss on ignition as shown for the average analyses of the ferruginous bauxite in Table I, and the constituents referred to above are increased proportionately to make up the total to 100%, the results obtained duplicate analyses of the ferruginous bauxites. The sample of dolerite from Narrabeen, referred to in Table IV, when treated this way gave exactly the average analysis given in Table I. Since the ferruginous bauxites and the rocks similar to the parent material from which they were derived contain the same proportion of alumina and ferric oxide, the writer is of the opinion that they are residual and not a metasomatic replacement of a residual deposit (MacLaren, 1906) or a mechanical replacement by material brought up from below (Campbell, 1909-10) or an efflorescence (Simpson, 1912). It must be considered extremely doubtful whether two constituents of different relative solubility could be introduced and the resultant product still maintain the same proportions of these constituents of the parent rock. Evans (1909-10) has suggested the term *katasomatism* for the process by which laterite is derived from the parent rock, instead of *metasomatism*, as the process is purely one of abstraction.

The clay underlying the ferruginous bauxite differs from it in containing less of the lateritic constituents and more silica. Also the bulk of the alumina is insoluble in a hot solution of sodium hydroxide. It contains the same relative proportions of alumina and ferric oxide as the ferruginous bauxite and basalt and is intermediate in chemical composition between them. A sample obtained from a shaft in one Emmaville deposit, immediately underlying the ferruginous bauxite, contained 3.5% alumina soluble in hot sodium hydroxide solution, 28.7% total alumina, 22.8% ferric oxide, 2.8% titania, 30.0% silica and 14.5% loss on ignition (including hygroscopic moisture).

From the above it is evident that in many cases the proportions of alumina and iron oxide are similar in the ferruginous bauxite, the underlying clay and parent rock.

Many different theories of the origin of laterites by weathering have been postulated, but they include the separation of the laterite into definite layers

as an essential feature of the process (Lacroix, 1913 ; Fox, 1927, etc.). These layers consist essentially of an upper one rich in ferric oxide and poor in alumina with a lower one rich in alumina and leached of iron oxide. Mohr (1930) and others also postulate that the silica leached from these layers was deposited below. Many of the New South Wales ferruginous bauxites, although thoroughly leached (millions of tons contain only between 2% and 3% silica and a large proportion less than 2% silica), show relatively little movement of the ferric oxide and no separation into an upper layer rich in iron overlying a lower layer leached of that constituent. Also, the writer has seen no definite evidence of the deposition of silica in the clay immediately underlying the bauxite. It is not intended to imply that all lateritic deposits in New South Wales show these features, but that there are some deposits whose origin cannot be fully explained by the theories previously put forward.

If the type of percolating solutions required for the formation of a typical ferruginous bauxite deposit in this state can be determined, much light will be thrown on the climatic and other conditions which prevailed at the time of its formation.

The removal of the potash, soda, lime, magnesia and other minor constituents can be easily explained. Daubree proved that water alone is a solvent for the potash in orthoclase. There are, however, differences of opinion as to the efficacy of various aqueous solvents for silica and iron. Mohr (1930) states : "The silicic acid of minerals is relatively most easily soluble in pure water (rain water), the presence of dissolved salts, or carbonic acid, or of organic materials decreases the solubility. Iron oxide and alumina are insoluble in pure water and in salt solutions, but go into solution as soon as the water contains humous organic materials or strong acids." On the contrary Moore and Maynard (1929) tested various solvents (including distilled water) on norite and diabase, demonstrating that the most effective for iron and silica is carbonated water, with peat-solution next in order. Oxygenated water was regarded as a very poor solvent for iron and only fair for silica. Iron and silica hydrosols, taken separately, were shown to be quite stable, but when mixed mutual precipitation occurred. They also demonstrated that a colloidal solution containing 30 parts per million silica and 10 parts per million ferric oxide remains stable, providing nine parts per million of organic matter are present, and that sea salt precipitates in 12 hours the greater proportion of the iron from the above solution, while the greater proportion of the silica is not precipitated until after four months. F. Weiss (1910) has shown that peat solutions can change impure clay to a residue of almost pure kaolin. Holmes (1914) records kaolin as an alteration product of granite, underlying a black damp soil, rich in organic material. The occurrence of fireclays underlying coal seams is quite common. The essential points common to these views are that :

- (1) Silica is soluble in the absence of organic material.
- (2) Iron can be held in solution in the presence of silica, only if organic matter be present.
- (3) With peaty organic matter in the percolating solutions the aluminosilicates are probably only partially decomposed to form kaolin, but not free alumina.

The formation of kaolin has been ascribed by Vageler (1933) to the presence of humic acid preventing complete hydrolysis of the silicates. The writer considers an equally likely explanation may be that complete decomposition of the silicates is only possible under oxidising conditions. Organic matter in the percolating solutions would give rise to reducing conditions leading to the formation of clay. The occurrence of clay underlying laterite, in parts of deposits where percolation had been inhibited owing to slumping (Mead, 1915)

and in temperate climates could all be regarded as being due to the poor supply of oxygen.

The formation of a typical New South Wales ferruginous bauxite deposit requires certain conditions. Complete leaching of the silica implies sufficient rainfall for the provision of an adequate quantity of percolating solutions, adequate drainage and probably absence of organic matter in the percolating solutions. On rocks potentially rich in mineral plant food, such as basalts, and on areas of gentle slope, such rainfall would provide an ample growth of vegetation. However, the stability of the iron oxide present in the ferruginous bauxites requires that the percolating solutions be free from dissolved organic matter. This is only possible where the leaf fall and other plant refuse can be rapidly destroyed by the attack of aerobic micro-organisms. This is impossible in a temperate climate and requires a warm temperature which favours microbiological growth. The writer is of the opinion that there are no special "laterite" bacteria at work, as suggested by Holland (1903), but merely that there is greatly enhanced activity of micro-organisms under warmer conditions. Campbell's (1909-10) suggestion that the restriction in altitude of laterites may be due to their porous nature rendering them very liable to the disintegrating action of frost, also favours a warm temperature for the formation of laterites generally. If the incidence of the rainfall is variable, the periods of light or no rainfall would allow more complete aeration and may result in more favourable conditions for the complete removal of silica. The rainfall could not be so plentiful as to support very heavy perennial vegetation, as this would lead to the accumulation of organic matter in the soil, notwithstanding the warmer temperature, resulting in movement of the iron and probably incomplete removal of the silica.

The occurrence of some high-grade bauxites means that conditions were suitable for the removal of iron in these instances. This could be brought about in a number of different ways. Firstly, the removal of iron may have taken place subsequently to the formation of a typical ferruginous bauxite deposit. The provision of the necessary organic matter in the percolating solutions would require either a lowering of the temperature to inhibit the activity of the micro-organisms in the soil or a more prolific growth or change in type of vegetation due to either heavier rainfall or a rising water table. Secondly the conditions favourable for the complete removal of the silica may have alternated with those suitable for migration of the iron oxide, being brought about by periodic variation in the climate. A third possibility is that when the leaching of the silica is almost complete, the amount of silica being taken into solution by percolating waters may be small enough to permit the stabilisation of ferric oxide hydrosols in solution without the presence of organic matter, thus allowing their removal. The surface layer of the deposit of high-grade bauxite at Sutton Forest has, in most places, a higher iron content than lower layers, but in no case was the iron content greater than that found in the ferruginous bauxites of the district. This means that there need not necessarily have been upward movement of the iron, but perhaps only leaching of the lower layers leaving the upper layer relatively unchanged. Van Bemmelen (1941) has recorded the occurrence of a layer high in iron oxide underlying a rich bauxite low in iron.

The upward movement of the iron in typical laterite deposits has been ascribed to capillarity, rising water table (Mohr, 1930) and electro-kinetic phenomena (Fox, 1928). The first explanation has been shown to be inadequate, but either of the others may explain the concentration of silica at the top of some New South Wales bauxites.

Before concluding it is necessary to discuss the manner in which the pisolitic, concretionary, nodular and vermicular structures were developed. These

structures were probably incipient during the early stages of the process of lateritisation, but the main development most likely took place at a late stage.

The pisolites in the ferruginous bauxites are either structureless or else the structures developed are concentric. In this they agree with the determinations of H. Schade (1909-10) and W. H. Bucher (1918), who have demonstrated that "concretionary bodies form when a substance passes from the state of an emulsoid to that of a solid, and that if the change leads to the crystalline state the resulting structure is radial if the substance is pure; if, however, other substances, colloid or crystalloid, are precipitated along with it a concentric structure is developed". What is considered to be incipient pisolitic structure was seen in a section of the clay derived by the weathering of basalt from Lorne, near Emmaville (see Plate II). Whitworth (1939) considers that the pisolitic structure is developed in some cases around the remains of altered olivine phenocrysts. In some cases pisolites, under the microscope, can be seen to be surrounded by a circle of other very fine pisolites. Some of these fine pisolites appear to have partly coalesced. A further development of this process may lead to the incorporation of the finer pisolites into the larger central one. In this way larger concretionary structures would tend to form at the expense of smaller ones. It is considered probable that the pisolitic structure is developed at or above water level and is built up gradually, minor fluctuations in water level allowing successive solution and redeposition. Banding in the structure (see Plate III), which gives an appearance of bedding, is probably related to variations in water level during successive periods of different duration.

The nodular type of surface weathering is well known. Decomposition, proceeding from joints in the mass, gradually results in rounded kernels of unweathered rock being left in an earthy or clayey matrix. The lateritisation of such material could easily give rise to a deposit of the nature of that at the Four-Mile (see Plate III), near Inverell. Complete destruction of the original rock texture and removal of the bulk of the impurities may lead to the development, at a later stage, of concretionary masses similar to those from Trundle.

At Lorne, near Emmaville, clay derived by the weathering of basalt has developed a vermicular texture (see Plate II). How this structure was first developed is only a matter of conjecture. J. W. Gruner (1922) has shown that in sections of olivine gabbro, peat solutions attacked the olivine preferentially and it had either been changed to an almost isotropic substance with a refractive index of 1.552 or had been eaten out entirely in a few places. It may be that the olivine phenocrysts in the basalt are preferentially leached and that later the pore spaces so formed become joined to form tubes. Many of our Tertiary basalts are amygdaloidal and the amygdules too, may be preferentially leached. Once tubular openings, however small, were formed, the relatively greater percolation along them would tend to increase their size, eventually giving rise to typical vermicular structure. Stronger leaching of the iron oxide around the tubes is well shown in material from the Sutton Forest deposit (see Plate II).

SUMMARY.

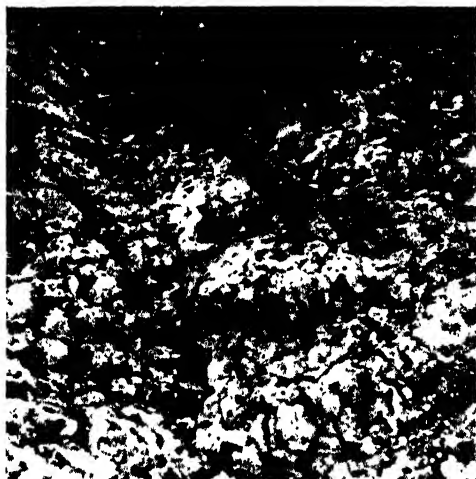
1. The New South Wales bauxite deposits can mainly be classed as ferruginous bauxites, although high-grade deposits occur, and are characteristically pisolitic, vermicular, nodular or earthy.

2. The mode of origin postulated is as follows:

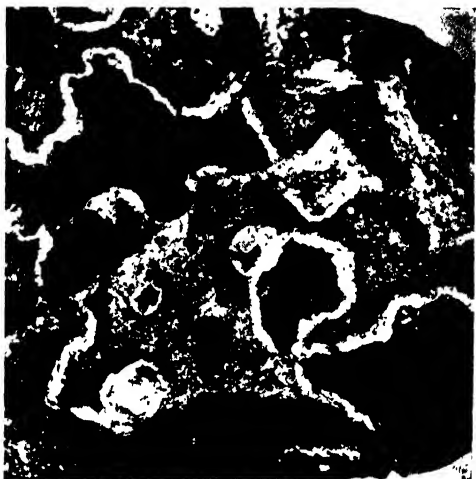
- (a) They were formed by the weathering of Oligocene basalts (except the Trundle deposits) during the Miocene period, on areas protected from mechanical erosion, and are true residual deposits, not replacements.



1



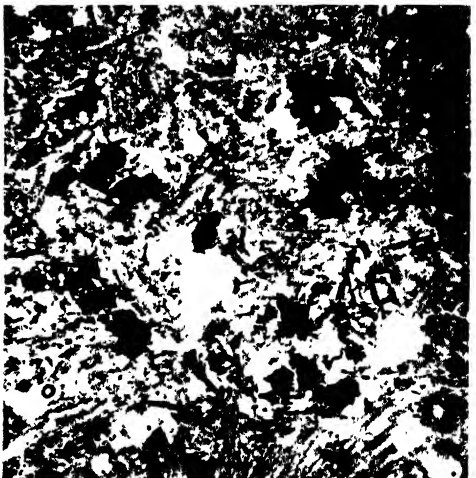
2



3



4



5



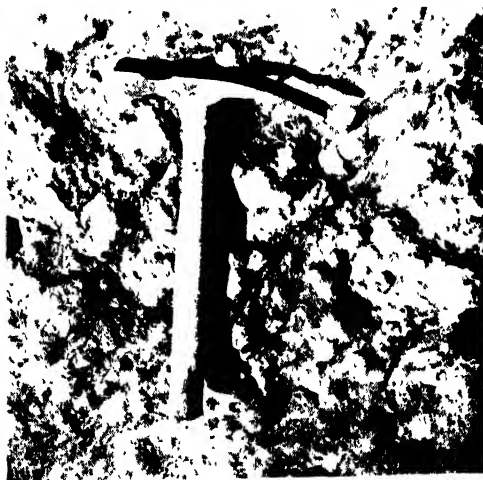
6



7



8



9

- (b) The lateritisation consisted in the removal of the alkalis and alkaline earths, with almost complete de-silication, but, in most cases, practically no removal of the iron.
- (c) The climate was probably warm, tropical to sub-tropical, and the rainfall moderate with possibly variable incidence, such incidence, however, not necessarily being either seasonal or divided into definite wet and dry periods.

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DESCRIPTION OF PLATES.

PLATE II.

Fig. 1.—View looking across the valley of the MacIntyre River towards the road to Copeton, taken from the Lookout near Inverell. Basalt outcrops as a continuous sheet from the high ground down over the cleared patch in the centre of the photo, to the valley floor. Granite outcrops in the trees to the left of the cleared patch.

Fig. 2.—Vermicular basalt in small gully below base of bauxite deposit at Lorne, near Emma-ville. The tubes are filled with iron-stained earthy material.

Fig. 3.—Photograph of sample of vermicular bauxite from Sutton Forest. The association of the lighter coloured material with the tubular openings is well shown. $\times \frac{1}{2}$.

Fig. 4.—Micro-section of sample of vermicular basalt shown in Fig. 3, illustrating what appears to be incipient pisolitic structure. $\times 250$.

Fig. 5.—Micro-section of bauxite nodule from Four-Mile near Inverell. The original outlines of the felspar laths can be seen. At present they consist of aggregates of gibbsite crystals. $\times 12$.

K—September 6, 1944.

PLATE III.

Fig. 6.—Photograph of quarry between Stannifer and Tingha. The shaft sampled is shown in the foreground, covered by wood. Photograph taken about midday in winter.

Fig. 7.—Photograph of quarry at Four-Mile, near Inverell. The shaft sampled is shown in the floor of the quarry covered by wood. The sampling cuts on the northern side and eastern end of the quarry are also shown. The surveyor's staff shown is 10 feet long.

Fig. 8.—Close-up of the face of the quarry shown in Fig. 6. The variation in the size and the banding of the pisolites can be seen. The Brunton compass shown at the bottom of the photograph was included as a scale.

Fig. 9.—Close-up of the face of the quarry shown in Fig. 7. The nodular structure is well shown.

THE DETERMINATION OF CALCITE AND ARAGONITE IN INVERTEBRATE SHELLS.

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INTRODUCTION.

It has been generally accepted for many years that certain invertebrate shells are essentially composed of calcite, whilst others are essentially aragonite. Small amounts of conchiolin and other calcium salts are of course always present, and also, in certain cases, magnesium salts. Calcite is the hexagonal form of CaCO_3 , and aragonite the orthorhombic form.

The presence of calcite or aragonite in invertebrate shells has some geological significance in the formation of certain limestone beds (Clarke, 1924) and is also of interest to zoologists in the study of shell deposition, environment, etc. Workers in these fields have used various methods for the differentiation of the two crystal identities, but in view of the metastability of aragonite, solubility differences due to varying particle size and the presence of organic matter and other salts, the purely chemical tests are considered unreliable under certain circumstances.

One of the most frequently used methods is that due to Meigen (1901, 1905). The test, which depends on the differences in solubility of calcite and aragonite, consists of boiling samples of the powdered material in dilute solutions of cobalt nitrate, when aragonite develops a reddish-violet colour, calcite remaining colourless, or becoming pale blue. This procedure is well known and has lately been used by Manigault (1939). While some results obtained by the method are confirmed by X-ray powder analysis, experiments will be described in this paper which show that calcite of sufficiently small particle size will yield the same result as aragonite. The effect of small traces of impurities, as well as variations in boiling time and strength of reagent, have also been investigated.

Another purely chemical test which has been investigated consists in treating the specimens with a solution of manganous sulphate containing silver sulphate, aragonite producing a black precipitate in from one to two minutes, the colour with calcite developing only after one to two hours (Feigl, 1939).

Of the other tests which have been used, little need be said. The differences in specific gravity and solubility in H_2CO_3 have been employed, but many of the results obtained thereby contain serious discrepancies (Cornish and Kendall, 1888; Cole and Little, 1911). Optical methods are available in many cases, and have been used for the determination of invertebrate shells (Trueman, 1942). It should be pointed out, however, that the inversion of aragonite to calcite does not necessarily involve actual morphological changes, and it is insufficient to classify crystals as aragonite on the basis of mere external symmetry.

EXPERIMENTAL.

Reference to literature published since Meigen's original papers on the subject reveals a singular lack of uniformity in the procedures recommended by various authors with regard to the cobalt nitrate reaction. The time of boiling varies from three to twenty minutes, and in most cases, no indication is given as to the strength of the cobalt nitrate solution which should be used. Moreover, the staining colours recorded by different authors cannot be reconciled, and in many cases are quite contradictory.

In the early stages of the work described herein, Meigen's original paper was not available to the author, and it was decided to study the effects of variations in reagent strength and boiling time.

Accordingly, the following solutions of cobalt nitrate were prepared: 0.31 M, 0.062 M, 0.031 M and 0.016 M. As the pH values of the solutions are important, these were determined, and found to be 5.3, 5.8, 6.2 and 6.3 respectively.

The technique adopted was as follows: Approximately 0.1 gm. of crushed specimen was placed in each of six test tubes and covered with 5 ml. of one of the cobalt nitrate solutions. They were then placed in a boiling water bath, and one removed every five minutes, so that the immersion time varied from five to thirty minutes. Immediately on removal the test tube was filled with water, the stained specimen washed several times by careful decantation, and then transferred with the minimum amount of water into a small porcelain crucible. After several minutes' settling, the water was carefully removed with a pipette. The colour was then observed against the white crucible, all colours being observed by daylight.

In nearly all cases a small amount of the specimen floated on the reagent, and after boiling either a blue or violet ring was observed round the test tube at this point, according as the mineral was calcite or aragonite. The bulk of this was removed in the decantation, the remainder adhering quite firmly to the tube, however, so that it did not vitiate the test. These coloured rings appear to be related to the concentration of CO_2 at the surface of the liquid.

Meigen's researches, subsequently referred to, indicated that in his experiments he added 1 g. powdered specimen with 100 ml. boiling water to boiling solutions of cobalt nitrate in Erlenmeyer flasks. The resulting solutions varied from 0.66 M to 0.16 M, and the boiling time ranged up to fifteen hours. This was to convert all the calcite or aragonite to cobalt carbonate, for chemical analyses. In publishing the results of this work, he recommended that the samples should be boiled from 10 to 20 minutes (Meigen, 1905).

The tests were first carried out on the powdered shells of *Saxostrea commercialis*. The results obtained are best presented in tabular form, and these are set out below.

TABLE I.

Shows staining produced by boiling powdered shells of *Saxostrea commercialis* in $\text{Co}(\text{NO}_3)_2$ of different strengths, with variations in time of boiling.

Concentration of Solution.	Time of Boiling and Colour Produced.					
	(1) 5 mins.	(2) 10 mins.	(3) 15 mins.	(4) 20 mins.	(5) 25 mins.	(6) 30 mins.
0.31 M	Pinkish lilac.	Lilac + light blue specks.	Pale mauve + blue specks.	Mauve + blue specks.	Mauve + blue specks.	Deeper mauve + blue specks.
0.062 M	Pink.	light mauve.	Mauve + blue specks.	Mauve, etc.	Deeper mauve, etc.	Same as (5).
0.031 M	Faint lilac pink.	Same as (1).	light mauve.	light mauve.	Deeper mauve.	Same as (5).
0.016 M	Pinkish mauve.	Mauve.	Mauve.	Deeper mauve.	Same as (4).	Same as (4).

On boiling powdered specimens of aragonite (pseudo-hexagonal from Molina, Spain) in the same set of solutions, a reddish-violet colour was developed in every case.

It will be seen from Table I that the staining produced could be taken as indicative of aragonite, but comparison with the above results shows that the colours were somewhat lighter

in shade than those developed by the genuine aragonite. Moreover, the results of the X-ray powder analyses indicate as shown below that the shell of this organism is composed exclusively of calcite :

Saxostrea commercialis.

- | | | | |
|--|----------------|---------|----------|
| (1) Porcellaneous layers from near base of shell—thickest cross section of porcellaneous layers. | Pt. Hacking | | Calcite. |
| (2) Nacreous layers from near base of shell—thickest cross section of nacre. | Pt. Hacking.. | | Calcite. |
| (3) Composite sample. | Pt. Hacking | | Calcite. |
| (4) Porcellaneous layers. | George's River | | Calcite. |
| (5) Nacreous layers. | George's River | | Calcite. |
| (6) Composite sample. | George's River | | Calcite. |

Cobalt nitrate tests on the shell of *Pecten medius* resulted in the development of a pale mauve colour, with numerous small blue spots, which rather suggested the presence of both aragonite and calcite. The powder photograph, however, indicated the presence of calcite only. Since less than 5% of impurity is detectable by the X-ray method, the likelihood of sufficient aragonite being present to materially affect the test was remote.

Certain of the species tested with cobalt nitrate by Meigen and Manigault were examined by the former's method, and also by X-ray analysis. The powdered specimens were boiled in a 0.062 M solution of reagent for fifteen minutes.

The specimens examined were *Distichopora*, *Pocillopora*, *Heliopora*, *Millepora*, *Helix aspersa*, *Spirula peronii* and *Terebratula caput serpentis*. All of these gave a violet colour with cobalt nitrate excepting the last mentioned, which assumed only a faint greenish tinge. On X-ray analysis, all were found to be aragonite except *T. caput serpentis*, which was calcite. These results were in complete agreement with Meigen's determinations. Of the above species *H. aspersa* was examined by Manigault (Manigault, 1939).

In order to ascertain the effect, if any, of the time which elapsed between the crushing of the specimens and their analyses, an additional sample of nacre of *S. commercialis* was crushed and immediately X-rayed. This sample, however, was also calcite. In addition, a portion of the genuine aragonite specimen from Spain under the same treatment revealed the true aragonite structure, thus indicating that the action of crushing and grinding could not have effected the inversion to calcite. From this it is evident that the cobalt nitrate tests on the shells of *S. commercialis* and *P. medius* were invalid. Tests carried out with Feigl's reagent also erroneously indicated the presence of aragonite.

Although chemical analysis indicates that the shells of *S. commercialis* contain 97.55% CaCO_3 , 1.48% organic matter and only 0.97% MgCO_3 , it was decided to study the effects of small amounts of MgCO_3 , $\text{Ca}_3(\text{PO}_4)_2$ and CaSO_4 . Accordingly, samples of pure calcite were crushed, and 2% of the above salts added. These were then treated with the cobalt nitrate solutions, and boiled for fifteen minutes.

TABLE II.

Showing the Effect on Meigen's Reaction of Small Impurities in Calcite.

Sample.	0.062 M.	0.031 M.	0.016 M.
Calcite (clear rhomb)	Pale blue.	Pale blue.	Very pale blue.
" (pseudomorph after aragonite)	Pale blue.	Pale blue.	Pale blue.
" +2% MgCO_3 (chemically prep.)	Pink + blue specks.	Pink + blue specks.	Pink + blue specks.
" +2% magnesite (MgCO_3)	Pale mauve + blue sp.	Mauvish pink.	Very pale pink.
" +2% apatite ($\text{CaF}(\text{Ca}_4(\text{PO}_4)_6$)	—	Very pale blue.	Bluish discoloration.
" +2% gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	Pale buff pink.	Very pale pink, very pale blue.	—

By carrying out similar experiments with Feigl's reagent, it was similarly observed that calcite with 2% of MgCO_3 also gave the aragonite reaction. At this stage of the work further experiments with Feigl's test were abandoned, as the reaction is regarded as too sensitive for use on shells, and requires also special precautions to ensure the absence of CO_2 from the reagent and atmosphere. No deeper staining was produced by cobalt nitrate when the content of MgCO_3 was increased to 15%.

The shells of *S. commercialis*, however, exhibit greater reactivity than the pure calcite, and this may be explained by the extreme smallness of ultimate particle size, which increases the rate of solution. Moreover, although the organic matter is thought to have no chemical effect, it is present as a matrix which is an integral part of the microscopic shell structure, and this undoubtedly increases its porosity. It was observed that the shells of *S. commercialis* and *P. medius* contained considerable areas of chalky material, whereas the shells of *S. peronii*, *H. aspersa* and *T. caput serpentis* contained practically none. The nacreous layers of *S. commercialis* are not quite as hard as even that of the calcite shell *T. caput serpentis*, and are much less resistant to attrition and comminution. This is attributed to the fact that the calcite crystals in *S. commercialis* are not firmly coherent, particularly in the chalky areas, which are very soft, and may result from colloidal precipitation, random orientation of particles perhaps being involved.

The above facts were demonstrated by immersing crushed samples of shell, aragonite and calcite for one hour in solutions containing 0.01% and 0.001% methylene blue, with subsequent washing. The calcite and aragonite were only very slightly coloured, whilst the shell was considerably stained.

Approximately 0.1 g. sample in 10 mls. solution :—

Calcite—

Methylene blue	0.01%	No colour
„	0.001%	Just discoloured

Aragonite—

Methylene blue	0.01%	Pale lavender blue
„	0.001%	Very faint blue

Shell—

Methylene blue	0.01%	Royal blue
„	0.001%	Lavender blue

Some of the intense colour of the shell is due to the dye attaching itself to the organic matter, but it must be remembered that this only amounts to 1.48%, and cannot be entirely responsible. Most of the colour is undoubtedly caused by the porosity of the shell, the dye being trapped in the cementation cracks of the somewhat loosely cohering calcite crystals.

Meigen reported (1905) that the degree of comminution of samples did not materially affect his test, except where large quantities of sample were taken. It is pointed out, however, that extreme fineness of particle size not only enhances solubility considerably, but also greatly increases surface area. Solution takes place most readily at particle corners and edges, and fragments may become more angular as the fineness of crushing increases (Gaudin, 1939). It is considered also that reaction takes place between the solid-liquid phases by surface absorption of cobalt nitrate and deposition of cobalt carbonates on the solid material. Thus, fineness of grinding will have a very big effect on the reaction. In any case, the samples used in the present work (0.1 g.) could hardly be called large, and the effect of smallness of crystal and fragment sizes is shown below.

Calcium carbonate was precipitated in gelatinous form from hot concentrated solutions of Na_2CO_3 and CaCl_2 . This was then filtered and carefully washed at the pump to remove all traces of soluble chlorides and carbonates. It was then transferred to a beaker, washed with boiling water several times by the decantation method (which caused complete precipitation) and dried at 50°–60° C. Two such preparations were made, one containing a trace of SO_4^{2-} , which was added to ascertain whether its presence would stabilise the aragonite structure if formed. When dry, samples were boiled in 5 ml. of 0.062 M cobalt nitrate for fifteen minutes. Both samples

gave a violet colour, identical with that produced by the aragonitic shells. In order to ensure that these samples were calcite and not aragonite, portion of one was left in its mother liquor exposed to the atmosphere overnight, and washed by repeated boilings and decantations next morning. It was then boiled in water for fifteen minutes, decanted and portion treated as above with cobalt nitrate. The same violet colour was produced, with darker specks. X-ray powder analysis four days later showed that both preparations were calcite. Further Meigen reactions carried out on the same samples showed, if anything, a slightly deeper colour, thus indicating that no falling off in reactivity or inversion had occurred.

By pulverising a shell of *S. commercialis* to a fragment size of -200 mesh and boiling in cobalt nitrate under the above conditions, a colour approaching amethyst was obtained. Pure calcite under the same conditions was coloured blue with a considerable amount of pink.

SUMMARY AND CONCLUSIONS.

It has been shown that Meigen's reaction and also that of Feigl for the differentiation of calcite and aragonite give erroneous results when applied to the shells of *Saxostrea commercialis* and *Pecten medius* taken from Sydney waters, although seven determinations by the former method have been verified by X-ray powder analysis.

Variations in reagent strength, boiling time and the presence of $MgCO_3$ all cause small cumulative errors in the cobalt nitrate method, while the presence of organic matter and $MgCO_3$ vitiates Feigl's test. With loosely cohering bodies of $CaCO_3$ of a cryptocrystalline or colloidal nature, or extremely comminuted fragments, both of these tests are definitely not specific for either aragonite or calcite.

If these tests are to be used, they should be applied with extreme caution, and not to samples of the abovementioned nature. It is probable that many invertebrate shells contain large quantities of chalky material, and the test should definitely not be applied to them. In any case, for shells which are nacreous and homogeneous throughout, the more certain physical tests are always available.

Finally, the author desires to emphasize the extreme metastability of aragonite, and the probability of variations from place to place even in a single species. So many factors can be involved in the aragonite-calcite system that the classification of whole genera and species of invertebrates on the examinations of a few specimens is unsafe. Without a comprehensive investigation of many specimens from all localities, it is considered that little can be done other than to record the crystal forms found in the different species at various places.

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QUATERNARY ARSONIUM SALTS AND THEIR METAL CO-ORDINATION COMPOUNDS.

PART I. BISMUTH.

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A number of metal compounds with quaternary arsonium iodides have been described previously, but no attention has yet been paid to the possibility of using them as reagents in the micro-detection or estimation of the metals concerned, for which, by reason of their large molecular weights they should be particularly suitable. The work described in this paper was carried out to determine their suitability for the detection and estimation of the metal bismuth.

Burrows and Turner (1921) have described addition products of the type $(\text{PhMe}_2\text{As})\text{MI}_3$ with iodides of phosphorus, antimony, bismuth and stannic tin; also similar products from PhMe_3AsI and iodides of cadmium, lead and mercury. Later (1926) they prepared $\text{PhAsHMe}_2 \cdot \text{BiI}_4$ by heating together the arsine, bismuth iodide, and excess of HI, and obtained a scarlet compound soluble with difficulty in hot concentrated hydrochloric acid, from which it recrystallised in scarlet plates.

In the present work, two series of methyl aryl tetra-iodo bismuthites have been prepared, and the effect of the substituent groups in the arsonium radical on the properties of the resultant tetra-iodo bismuthites studied, with special reference to the sensitivity of the reaction.

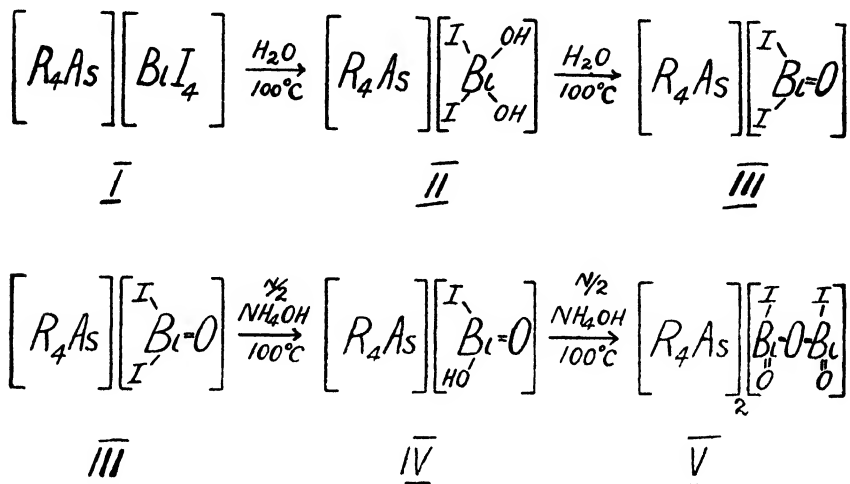
The compounds were insoluble in water, soluble in hot $\text{N}/2 \text{ HCl}$, the solubility decreasing rapidly as the molecular weight increased, being less than one part in a thousand in the case of $p\text{-tol}_3\text{MeAsBiI}_4$. The compounds were quite soluble in hot alcohol. The colours changed progressively from brick-red to yellow as the molecular weight increased, while the $p\text{-tolyl}$ derivatives in each case were lighter than the corresponding phenyl derivatives.

The melting points also decreased with increasing molecular weights, with the exception of $((\text{C}_7\text{H}_7)_3(\text{CH}_3)\text{As})(\text{BiI}_4)$, which had a melting point higher than $((\text{C}_7\text{H}_7)_2(\text{CH}_3)_2\text{As})(\text{BiI}_4)$ and $((\text{C}_6\text{H}_5)_3(\text{CH}_3)\text{As})(\text{BiI}_4)$.

The sensitivities of the quaternary arsonium iodides for the detection of bismuth reached the maximum near the middle of the series, owing to the fact that as the molecular weight increased, decreasing solubility was compensated by decreasing intensity of colour. Contrary to expectation, the $(\text{C}_7\text{H}_7)(\text{CH}_3)_3\text{AsI}$ is the most sensitive, being probably due to the fact that, although it is almost as deeply coloured as the compound with $(\text{C}_6\text{H}_5)_3(\text{CH}_3)_3\text{AsI}$, the para methyl group depresses the solubility out of proportion to its contribution to increase to molecular weight. The reagents at present used for the detection of bismuth include thiourea (Sensi and Seghezze, 1929) which will detect $10\gamma/\text{ml.}$ and cinchonine iodide (Feigl and Neuber, 1923) capable of detecting $3\gamma/\text{ml.}$ All of the arsonium iodides used in this study were superior to both of these reagents, whilst the best, $(\text{C}_7\text{H}_7)(\text{CH}_3)_3\text{AsI}$, is twenty times as sensitive as thiourea, and six times as cinchonine iodide.

These R_4AsBiI_4 compounds readily underwent hydrolysis, partially in cold water, and completely in boiling water, to the compound $R_4AsBiOI_2$ (III), which could be readily reconverted to the compound R_4AsBiI_4 by boiling with dilute hydrochloric acid and a small amount of R_4AsI . The partially hydrolysed compound can be further hydrolysed, by boiling with N/2 ammonium hydroxide, to the final possible hydrolysis compound, $(R_4As)_2(Bi_2O_3I_2)$. When, however, the compound R_4AsBiI_4 was boiled with N/2 ammonium hydroxide, instead of the final hydrolysis compound being formed, complete breakdown to bismuth oxide occurred, whilst a smell of tertiary arsine could be detected.

It was considered that these reactions proceeded as follows :



The intermediate compounds (II) and (IV) were too unstable to be isolated, and their formation was probably only transitory. It was considered that the inability of the compound (I) to be transformed directly to (V) by boiling with N/2 ammonium hydroxide is due to the fact that the required intermediate $(R_4As)(Bi(OH)_3I)$ (VI) either cannot be formed or is extremely unstable, and hence the hydrolysis must be carried out in two stages as shown above.

With the exception of the well-known BKI_2 , these hydrolysed compounds have not been previously described.

EXPERIMENTAL.

The quaternary arsonium iodides were made from the corresponding tertiary arsines by refluxing with a slight excess of methyl iodide in alcoholic solution. They were precipitated by the addition of a large excess of ether, and recrystallised by dissolving in the minimum amount of alcohol, and reprecipitating with ether. The bismuth nitrate solutions were prepared by dissolving C.P. bismuth tri-oxide in the minimum amount of nitric acid with warming.

Phenyltrimethylarsonium tetra-iodo bismuthite. $(C_6H_5)(CH_3)_3AsI$ (1 gm.), potassium iodide (1 gm.) and sulphuric acid (0.5 ml.) were dissolved in water (400 ml.) with warming. (More water is needed in the case of the higher quaternary arsonium iodides.) To this solution was added in a thin stream with rapid stirring a solution of bismuth nitrate (equivalent to 0.4 gm. Bi_2O_3). This is approximately equivalent to 0.5 gm. of the arsonium iodide; the excess of the latter was considered necessary owing to the fact that any excess of bismuth would lead to the formation of the highly insoluble $KBiOI_2$. The fact that the compound R_4AsBiI_4 was formed in preference is obviously due to its greater insolubility. The use of the quaternary arsonium iodides for the quantitative estimation of bismuth, and other metals, for example cadmium, will be the subject of a subsequent communication. The arsonium tetra-iodo bismuthite separated as a fine red precipitate, which coagulated on continued stirring, leaving the supernatant liquid

quite clear and colourless. The crystalline compound was readily filtered with suction, recrystallised from N/2 hydrochloric acid, to prevent hydrolysis, in the presence of $(C_6H_5)_3(CH_3)_3AsI$ (0.2 gm.), washed with N/2 hydrochloric acid, and dried in a desiccator over calcium chloride and calcium hydroxide. The compound was analysed as follows: The iodine was estimated by the method of Dwyer and Nyholm (1942). Arsenic was estimated by the chromic acid method of Anderson and Burrows (1936). It was noted that in this estimation, when the chromium is precipitated, the solution should be made definitely alkaline with sodium hydroxide, and boiled to decompose the sodium chromite to chromic hydroxide, otherwise the arsenic is precipitated as the basic chromium arsenate, and a low result is obtained. Bismuth was determined by fuming the compound with sulphuric acid and potassium nitrate, precipitating the resultant bismuth salt as the cupferron complex, and igniting to the oxide. This gave a high value, owing to co-precipitation of the arsenic, so the ignited precipitate was dissolved in nitric acid, reprecipitated as the oxalate and the latter titrated with standard potassium permanganate.

Found: As=8.17%; Bi=22.5%; I=56.1%. Calculated for $((C_6H_5)_3(CH_3)_3As)(BiI_4)$: As=8.21%; Bi=22.9%; I=55.6%.

Diphenyldimethylarsonium di-iodo-oxy-bismuthite. This was produced by boiling $((C_6H_5)_3(CH_3)_3As)(BiI_4)$ three times in distilled water, grinding up any lumps formed in the process. The light chocolate powder was filtered and dried over calcium chloride.

Found: I=34.2%. Calculated for $((C_6H_5)_3(CH_3)_3As)(BiOI_3)$: I=34.4%.

Bis-diphenyldimethylarsonium di-iodo dioxy-μ-oxy dibismuth (V). This was prepared from the previous compound (III) by grinding to a fine powder, suspending in N/2 NH_4OH , boiling for half an hour, and filtering. The pale red-brown powder was dried over calcium chloride.

Found: I=20.6%. Calculated for $((C_6H_5)_3(CH_3)_3As)_2(Bi_2O_5I_2)$: I=20.5%.

Sensitivity. The sensitivity tests were carried out as follows: The standard bismuth nitrate solution was prepared by dissolving bismuth oxide (0.1117 gm.) in 15N nitric acid (approximately 18 ml.), and diluting to 100 ml. This solution contained 1.0 mgm. or 1,000 γ of bismuth per ml., and was 2.5 N with respect to nitric acid. It was diluted 100 times to give a stock solution containing 10 γ Bi/ml. and N/40 with respect to nitric acid.

The quaternary arsonium iodide solutions were prepared by dissolving 0.5 gm. R_4AsI , 0.5 gm. KI, 0.2 ml. H_2SO_4 (36N) and 0.2 ml. H_2SO_3 (5% free SO_2) in 100 ml. of aqueous solution. Owing to low solubility, a saturated solution of $(C_7H_7)_3(CH_3)AsI$ was used. The sulphurous acid was introduced to suppress aerial oxidation of the iodide to iodine, which gives a precipitate of the triiodide on standing.

The sensitivity tests were carried out in half-inch test tubes, 1 ml. of the bismuth nitrate solution being pipetted in first, then 1 ml. of the arsonium iodide solution. The resultant test was viewed in artificial light directed at right angles to the line of vision. The R_4AsBiI_4 compounds at the concentrations observed appeared as an orange opalescence, with a faint green fluorescence, which was not observable at higher concentrations. The sensitivities are summarised in Table I.

TABLE I.

Compound.	M.P. of Arsonium Iodides.	M.P. of Bismuth Compounds.	Colour.	Iodine. (Theor.)	Iodine. (Found.)	Sensitivity γ/ml.
$((C_6H_5)_3(CH_3)_3As)(BiI_4)$..	244° C.	171° C.	Deep red.	55.6%	56.1%	1.0
$((C_6H_5)_3(CH_3)_3As)(BiI_4)$..	191° C.	161° C.	Reddish orange.	52.0%	52.0%	0.7
$((C_6H_5)_3(CH_3)_3As)(BiI_4)$..	173° C.	80° C.	Light orange.	49.1%	49.2%	0.8
$((C_6H_5)_3(CH_3)_3As)(BiI_4)$..	269° C.*	124° C.	Red.	54.8%	54.7%	0.5
$((C_6H_5)_3(CH_3)_3As)(BiI_4)$..	178° C.	77° C.	Orange.	50.6%	50.7%	0.6
$((C_6H_5)_3(CH_3)_3As)(BiI_4)$..	175° C.	103° C.	Orange yellow.	47.1%	47.6%	0.8
$((C_6H_5)_3(CH_3)_3As)(BiOI_3)$..	—	—	Light chocolate.	34.4%	34.2%	—
$((C_6H_5)_3(CH_3)_3As)_2(Bi_2O_5I_2)$..	—	—	Pale red-brown.	20.5%	20.6%	—

Where C_6H_5 =phenyl.

C_7H_7 =p-tolyl.

* Rayziss and Gavron, "Organic Arsenical Compounds", gives M.P.=247.5° C.

SUMMARY.

The use of quaternary aryl alkyl arsonium iodides for the micro-detection of bismuth has been investigated, and it has been shown that these compounds can be used to detect bismuth in concentrations of less than 1γ of bismuth per millilitre of solution, p-tolyltrimethylarsonium iodide giving a reaction down to $0.5\gamma/\text{ml}$.

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THE STERNAL INTEGUMENT OF *TRICHOSURUS VULPECULA*.

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With Plates IV-VII.

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The skin of the newly born young of *Trichosurus vulpecula*, the common or grey Australian possum, presents a homogeneous unpigmented appearance up till two months of age. In the third month of its life in the pouch a grey pigmentation appears on the skin of its dorsum which within a few weeks deepens and frequently appears as an almost black discoloration. This is in marked contrast to the ventral aspect, which is unpigmented with the exception of a narrow median band of grey situated over the sternum. Towards the end of the third month it becomes evident that the pigmented skin on both the dorsal and ventral aspects of the body is covered by grey or black hairs and that the unpigmented areas are covered by white hairs alone. The pigmented sternal strip at this stage is approximately of equal width in the two sexes (4-8 mm.). In the female it is about 25 mm. long, while in the male it extends further up the neck and is about 35 mm. long (Figure 1). The grey hairs on this area are not obvious during the fifth and sixth months of life, partly because the light hairs on the ventral surface pass through a period of yellow coloration (Bolliger and Carrodus, 1940). After the replacement of these yellow hairs by white ones during the seventh or eighth month of life the sternal hair fibres are distinguished from those elsewhere on the venter by their grey colour and coarser texture. Between the eighth and twelfth months these grey sternal hairs in both sexes begin to assume a brown colour along the whole length of the shaft, a process more pronounced and rapid in the male than in the female.

It is mainly this sternal skin area, covered by its distinctive hair fibres, which forms the subject of the present investigation. In many animals, notably the fully grown male, this region is further characterised by a moist and frequently copious secretion with a distinct but not disagreeable odour. It seemed reasonable to suppose that some special glandular activity in the skin was responsible for this, and consequently not only the hairs but also the underlying skin were examined in detail.

MATERIAL AND METHODS.

Over a hundred specimens of *Trichosurus vulpecula* of all ages obtained from many different localities of eastern New South Wales have been examined. Skin from the sternal region and other parts of the body of four adult males and four adult females, obtained immediately after the animals were killed, was fixed in 10% formalin. Serial sections parallel to the surface of the skin were

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prepared by the method described by Carter (1939). These were stained with hæmatoxylin, eosin and picric acid. In a limited number of cases sections perpendicular to the skin surface were also made. Skin from three pouch young was also obtained and treated in a similar manner. Whole mounts of fibres were made for the detailed study of fibre structure.

MORPHOLOGY.

In order to discuss the peculiarities of the sternal integument it will be necessary to compare it with that on other parts of the body. It is convenient to describe first the general external appearance of the skin and hairs as seen in the living animal, and then the histological features of the underlying skin structures as studied in serial sections.

External Appearance.

(1) *Integument in General.* The skin of the adult is unpigmented. The body is covered with a dense, rather woolly coat of fur, there being from 75 to 300 hairs to the square millimetre, varying with the individual and the body region examined. The length of the individual hairs varies considerably, but the average length of hairs in most animals is between 2 cm. and 3 cm. Two types of hair may be distinguished: (a) long, thick and straight hairs which project beyond the rest of the fur, and (b) shorter, fine and wavy hairs which are much more numerous and form a dense underfur. The first type are grey or white in the proximal half. The thicker distal half is generally dark brown or black in hairs from the back, and white in hairs from the belly. A medulla is generally continuous along the major portion of the fibre, but is absent from the extreme tip and is discontinuous at the base. Hairs of the second type show considerable variation in length, but there is a continuous gradation from the shortest to the longest fibres. The longest ones have a thickened tip which is bent at an angle to their main axis. All hairs of type (b) have a more or less crimped appearance similar to that of sheep's wool. They are all grey or white in the proximal half and those of the back are brown or black in the distal half, while those on the belly are white. On the back the longest hairs of this type generally have a white band in the thickened portion near the tip. The hairs are usually medullated over most of their length, but the attenuated tips and frequently the bases at epidermal level are without a medulla. In older males on limited and varying areas over the thoracic part of the back the bases of all types of hair may have a light yellow-brown colour.

In a small number of possums, pigment may be entirely lacking from the hairs of all parts except the sternum. These animals though white are not however true albinos.

(2) *Sternal Area.* The skin is unpigmented here as elsewhere. In juvenile and fully grown possums all the hairs on the sternal area are short, thick and fairly straight. Their average length is 5-10 mm. They are more sparse than those on the surrounding areas, and their slope caudally may be clearly seen. In this region it is not easy to discern the two main hair types which are found on other parts of the body, although histological studies indicate that the same two types of hair follicles are present here as elsewhere. In the adult all the hairs are a reddish-brown due to the presence of pigment in both cortex and medulla. The extreme tips of the fibres are without medulla or pigment but elsewhere within the shafts the pigmentation is very uniform.

Even specimens of the white variety of *Trichosurus vulpecula* which lack pigmentation on the rest of the body except the eyes have a typically pigmented sternal area.

The area of skin covered by these hairs differs in the two sexes after reaching maturity. In the female it may measure about 5-7 cm. in length and 1-3 cm. in width. In the fully grown male it may measure 8-10 cm. in length with a maximum width of 3-5 cm. Though there are fairly wide variations in the size of the sternal area of different possums the average dimensions in the male are definitely greater than those in the female. The male sternal patch is also characterised by its shape, which, due to lateral extension at the level of the forelegs, frequently takes on a triangular or diamond shape. Cephalad it usually extends along the ventral neck in a broad band while the female sternal patch extends cephalad only as far as the end of the sternum (Figures 2 and 3).

Skin Histology.

Unfortunately no detailed description of skin structure in the possum has been published. De Meijere (1894) devoted one paragraph to the arrangement of hairs in groups and bundles, and Gibbs (1938) gave a full description of the arrangement of hairs in the pouch young but did not describe the adult appearance. Neither author mentioned the modified sternal area. It will therefore be necessary to describe general skin structure in some detail.

(1) *General Integument.* The epidermis of the adult possum consists of a thin stratum corneum and a thin stratum malpighi, the latter having about four layers of cells. No trace of pigmentation could be seen in the epidermis.

The dermis is about one millimetre or less in thickness and consists mainly of a network of collagen fibres which pass between and below the groups of hair follicles and associated structures extending into the dermis. There are no papillae projecting into the epidermis, and pigment was not seen.

The hairs are arranged in groups (Figure 4), each group consisting of a central, more or less thick hair and two or more lateral clusters of finer hairs. Occasionally a central hair follicle stands alone or is accompanied by only one lateral cluster. In the deeper portions of the dermis each fine hair of the lateral clusters has its own follicle but near the skin surface the adjacent follicles of each cluster unite to form a common follicle. The follicle of the central hair stands alone and generally has a separate opening on the skin surface, but occasionally one or two of the finer hair follicles unite with it near the surface. Each central follicle has a sebaceous gland and a sudoriferous gland associated with it, while each lateral cluster has a sebaceous gland but no sudoriferous gland. The absolute and relative sizes of the two types of hair follicles, the number of lateral clusters per central follicle and of hairs in each cluster, and the total density of follicles in the skin may vary considerably between individuals and between body regions.

Each central follicle extends deep into the dermis and forms a more or less acute angle with the skin surface.¹ A follicle papilla of dermal origin and inner and outer root sheaths are present. The inner root sheath is keratinised and continuous with the stratum corneum superficially but in the deeper layers its nucleated cells closely surround the fibre. The outer root sheath has only about two layers of cells. The hair fibres are round or oval in cross-section, and possess a cuticle and cortex with or without a medulla at skin level. Pigment, which is confined to the cortex and medulla of the hair, varies according to the age of the specimen and the body region examined. There is also considerable variation even between adjacent fibres in the occurrence of pigment. Some central follicles may be involuted, the fibres being absent.

¹ Structures within or close to the acute angle formed by the follicle and its perpendicular projection on the skin surface are referred to as lying on the acute aspect of the follicle, while those within or close to the obtuse angle so formed are referred to as lying on the obtuse aspect of the follicle.

Each central follicle has a sebaceous gland and a sudoriferous gland opening into it.

The lateral clusters of follicles lie parallel to and on either side of the central follicles. Individual lateral follicles extend to various depths in the dermis but generally are not so deeply implanted as the central follicle of the group to which they belong. In the deeper levels the inner root sheath is similar to that of the central follicle. In the common follicle opening the nucleated inner root sheaths may continue to surround each fibre, or they may be replaced by keratinised epithelial fragments scattered between the fibres. The outer wall of the common follicle is similar in structure to the stratum malpighi and continuous with it. Directly below this each fibre has its own follicle sheath, in which the outer root sheath is very thin, the follicles being packed tightly together. Still deeper, the individual follicles become quite distinct, although still close together, and each has its own root sheaths and papilla. The fibres are fine, and round or oval in cross section. Pigment may or may not be present in the cortex, as in the central fibres. A medulla, which is less frequently present than in central fibres, may contain pigment. At the level where the follicles of a cluster are most closely packed together, they are surrounded by a mass of sebaceous gland tissue. No sudoriferous glands are associated with the lateral clusters.

Fragments of smooth muscle which might represent rudimentary arrector pili muscles are seen in the dermis, but their attachment to follicles or connective tissue sheaths has not been seen. Gibbs (1938) described an arrector pili muscle attached to the connective tissue sheath around each follicle group in pouch young.

The sebaceous gland accompanying each central follicle is of the simple acinous type and forms a collar of tissue surrounding the upper part of the follicle. The most superficial part of the gland opens directly into the follicle from the acute aspect. This opening is deeper in the skin and on the side of the follicle opposed to the opening of the sudoriferous duct. Slightly deeper in the skin there may be a second sebaceous gland opening from the obtuse aspect (i.e. on the same side of the follicle as the sudoriferous duct opening). The sebaceous glands show the characteristic appearance of active holocrine glands, with cells undergoing decomposition in the formation of secretion. Masses of eosinophilic secreted material may be seen at the gland opening and in the hair follicle mouth.

The collar of sebaceous gland tissue surrounding each lateral follicle cluster is slightly deeper in the skin than that of the central follicle. The opening into the common follicle mouth is at the most superficial end of the gland and on the acute aspect of the follicle. This gland shows the same signs of activity as the central follicle sebaceous gland.

The sudoriferous gland accompanying each central follicle is a simple coiled tube and its activity is essentially of the apocrine type (Schiefferdecker, 1917). The gland lies beside a follicle group in the dermis and its duct opens into the upper portion of the central follicle just below the opening of the latter on to the skin surface, and on the obtuse aspect. The duct is a slender tube passing through the dermis and its course is straight or only slightly sinuous. It lies beside the central follicle on the obtuse aspect. The wall of the duct is of uniform thickness and consists of one layer of a connective tissue sheath and two layers of undifferentiated epithelial cells with flattened nuclei. The lumen is very narrow, and no secreted material has been seen in it. The transition between the duct and the secretory portion of the gland is effected by a gradual widening of the lumen and a marked change in the nature of the lining epithelial cells. The secretory portion takes the form of a wide unbranched tube ending blindly and arranged in four or five loose coils. It lies beside the central follicle papillæ.

The wall of the gland consists of three layers: (i) a single layer of connective tissue cells surrounding the gland, (ii) a layer of myo-epithelial cells in various stages of contraction, (iii) a single layer of secretory epithelium whose cells vary in shape according to the stage in the cycle of apocrine gland secretion (Schieffer-decker, 1917). They may be flattened, cubical, subcylindrical or cylindrical with irregular cytoplasmic processes extending into the lumen. The flattened type is the most common. The lumen is generally empty but eosinophilic colloidal or granular material is occasionally present. When the myo-epithelial layer is contracted the lumen decreases in size. Histological examination suggests that at least some of these sudoriferous glands are active.

(2) *Sternal Integument.* An examination of skin sections from the sternal region shows that here the position and arrangement of the various structures is essentially similar to that on other parts of the body, but that there are clear differences in both absolute and relative sizes of certain parts, and in the apparent degree of activity of the glands. Some of the differences will now be described. A summary of the main quantitative differences in a comparison between the back and sternal regions of a single male specimen is given in Table 1.

On the sternum the skin is 50 per cent. to 100 per cent. thicker than elsewhere on the body. This is due to a slightly thicker stratum malpighi and a very much thicker dermis. The epidermis is again unpigmented. The dermis is similar in structure to that of the general skin.

The hair follicles are grouped in the same manner as elsewhere on the skin (Figure 5) but the number of lateral clusters per central follicle and the number of fibres per lateral cluster is appreciably lower than on any other body region examined. The number of groups per unit area is also low. A small lateral cluster often has a common follicle opening with the central follicle. The follicles are more deeply implanted on the average than in other regions and the average fibre thickness is greater. The follicles extend obliquely into the skin as on other regions.

The outer root sheath of the central follicles is somewhat thicker than on other regions, but the inner root sheath is very similar. The hairs of the central follicles are almost invariably medullated. Yellow or brown pigment is always present in the medulla and sometimes in the cortex.

The inner and outer root sheaths of a lateral cluster follicle are more distinct from those of adjacent follicles at sebaceous gland level than they are on other parts of the body, probably due to the fact that on the sternum the follicles of a cluster are not so tightly packed together in the skin. Medullation is more common on the sternal region than elsewhere.

As in other regions, no definite arrector pili muscle could be distinguished.

The sebaceous glands accompanying both central follicles and lateral follicle clusters are extremely large and apparently very active. That surrounding the central follicle has one or two openings in the usual positions. Large areas within the body of the gland are filled with secretory material, the cells having broken down. Eosinophilic secreted material is also seen in quantities at the gland openings and in the hair follicles superficial to this level. The sebaceous glands of the lateral follicle clusters open widely into the common follicle near their superficial end in the acute dermal area. Deeper there are one or more openings on the obtuse aspect of the follicle. These openings are either into individual follicles or into the common follicle. The glands show the same signs of activity as do the central follicle sebaceous glands.

The sudoriferous gland accompanying each central follicle is very much larger and apparently more active than those on the general body surface. The duct is much thicker and varies in diameter along its length. At its opening into the central follicle is a dilatation lined with epithelium similar to and continuous with the stratum corneum and stratum malpighi. Below this the

TABLE 1.

Comparison of Quantitative Characters of the Skin of Dorsal and Sternal Regions in Possum No. 400 (Adult Male).

Character.	Dorsum.	Sternum.
Thickness of epidermis	24 μ	28 μ
Thickness of stratum corneum	12 μ	12 μ
Thickness of stratum malpighi	12 μ	16 μ
Number of cell layers in stratum malpighi ..	3	4
Thickness of dermis	1 mm.	2 mm.
Number of lateral clusters of hair follicles about each central follicle.	2-4	0-4
Number of follicles per lateral cluster ..	Average 3	Average 2
Number of lateral follicles per central follicle ..	1-11	2-8
Number of central follicles per square millimetre	Average 8	Average 6
Total number of follicles per square millimetre	Average 17	Average 12
Average diameter of hair at levels ..	Average 5-1	Average 2-5
Sebacious glands of central follicles :	Average 85	Average 30
Depth	17 μ	32 μ
Width	Max. 80 μ	Max. 650 μ
Sebacious glands of lateral clusters :	Max. 70 μ	Max. 300 μ
Depth	Max. 90 μ	Max. 700 μ
Width	Max. 70 μ	Max. 250 μ
Sudoriferous gland duct, external diameter (major axis).	About 20 μ	180 μ superficially (dilatation). 70 μ at base of dilatation, decreasing gradually to 50 μ , then increasing to 70 μ .
Internal diameter (major axis)	Very narrow.	Up to 150 μ in dilatation, 24 μ decreasing to 10 μ , increasing to 35 μ in duct.
Thickness of duct wall	One layer connective tissue. Two layers flattened epidermal cells.	Dilatation lined by stratum corneum and stratum malpighi. Superficially, duct proper has 6-7 layers of epidermal cells, the innermost partially keratinised. Decreases to 4-5 layers. Decreases to 2 layers epidermal cells connective tissue sheath.
Content of lumen	—	In reservoir and duct, occasionally eosinophilic secretory material. Occasionally crystals in male.
Secretory portion of sudoriferous gland :		
Size of gland mass	To 500 μ long. To 170 μ wide.	To 1,100 μ long. To 700 μ wide.
Width of lumen	To 150 μ .	To 500 μ .
Wall thickness	To 12 μ .	To 14 μ .
Activity judged by secretory epithelium..	Some glands appear to be active.	Most glands appear to be very active.
Content of lumen	Eosinophilic material occasionally present.	Eosinophilic material frequently present. Crystals in male.

width of the lumen and of the duct decrease gradually; here the wall consists of six or seven layers of epithelial cells similar to those of the stratum malpighi, the innermost layer of cells being flattened and partially keratinised. At the middle of the sebaceous gland level in the skin the lumen is at its narrowest and the flattened cells become replaced by a layer of more cubical cells whose cytoplasm is strongly eosinophilic and bears fine inwardly directed projections. Below this the thickness of the gland wall decreases to four or five cell layers. In the deepest part of the sebaceous gland stratum the thickness of the epidermal part of the wall decreases to two cell layers, and a connective tissue sheath becomes clearly distinguishable. Eosinophilic secretory material has been found both in the dilated opening and in the duct proper. The lumen of the duct widens rather suddenly into the secretory portion of the gland, and at the same time the character of the innermost cells changes. The secretory portion (Figures 6, 7) is a wide unbranched tube ending blindly and forming a large mass of loose coils. It is situated deep in the dermis at and well below the level of the hair follicle papillae, and lies beside central and lateral hair follicles. The three typical cell layers are present in the wall. The myo-epithelial cells are generally relaxed. The secretory epithelial cells frequently assume the cubical and cylindrical rather than the squamous form, and cytoplasmic processes into the lumen are very numerous. The tips of these processes are sometimes basophilic. The lumen is sometimes empty, but eosinophilic colloidal or granular material is frequently present. Some of this material shows traces of cellular origin. The general picture appears to be one of marked activity. Perhaps the most significant result of the examination of sternal skin was the discovery of crystals in the lumen of the sweat glands of the sternal region. These were yellow, rod-shaped crystals with oblique or square ends; they varied considerably in size. They have been found in the sweat glands of the sternal region of four male adult possums but were not seen in the corresponding region of four adult females. Nor have any such crystals been seen in any other body region either in males or in females. Crystals were seen most commonly in the lumen of the secretory portion of the sudoriferous glands (Figures 6, 8), where the rods tended to form rosettes, and were frequently associated with eosinophilic secretory material. Clumps or rosettes of crystals were also seen in the lumen of many gland ducts, both in the terminal reservoir and in the duct proper (Figure 9). Here again the crystals were frequently associated with eosinophilic material. The only other site of crystal formation which has been found is the wall of the secretory portion of the glands, where scattered rods were sometimes to be seen, most frequently in the connective tissue layer (Figure 10). A blood capillary was often seen near the gland wall not far from a crystal deposit. The crystals seen were yellow even in unstained sections, but their colour seemed to be enhanced by picric acid staining. They were sparingly soluble and birefringent. From this and other evidence to be published later, it is believed that they were urates.

It seems definitely established that the crystals have been formed in the course of secretion by the sudoriferous glands, but it is likely that this particular substance is not synthesised within the secretory cells.

(3) *The Histology of Sternal Skin in Pouch Young.* The general features of the histology of the skin in pouch young which were described by Gibbs (1938) were confirmed in the present study. In addition to our observation on adult *Trichosurus vulpecula*, a comparison was made between the sternal region and other parts of the body in three male pouch young. The first of these measured 16.0 cm. from the tip of the snout to the root of the tail, and was about two months old, i.e. in the unpigmented stage mentioned at the beginning of this paper. The sternal area was at about the same stage of development as the back and belly, with groups of three, four and five follicles of which the

central one contained a keratinised fibre. No pigmentation of skin or fibres was seen in any of these regions. There was a sudoriferous gland accompanying each central follicle, but the terminal expansion had not yet developed. The sudoriferous glands on the sternal area extended as deep into the skin as the central follicles, while those on the back and belly did not extend so far. A sebaceous gland had begun to develop beside each central follicle on all areas, but only on the sternal area could sebaceous glands accompanying lateral follicles be distinguished.

The second specimen was 17.9 cm. long, and was about 100 days old, i.e. in the stage where dark hairs cover the back and sternum. Here fibre development on the sternum was slightly ahead of that on the back, and most of the fibres on both areas were pigmented. Sudoriferous glands were slightly further developed on the sternum than the back and the terminal expansion which later gives rise to the secretory portion was just visible in the former region. Sebaceous glands had developed in association with the central and most lateral follicles and these also were slightly further developed on the sternum.

The third specimen was 27.6 cm. long, and its age was estimated at seven months. Its ventral fur was in the transitory stage of yellow coloration referred to earlier. In this specimen skin development had reached a more advanced stage than in any of the animals examined by Gibbs, there being about nine fibres developed to each group on the back. In this region the terminal expansion of the sudoriferous glands had begun, but on the sternum the development was further advanced, and the secretory portion was forming coils in the dermis. By comparison with those on the back, the sebaceous glands in the sternal region were very large and well developed.

Thus it is clear from these few observations that while the general course of skin development in the sternal region is similar to that on other parts of the body, the main features which distinguish the sternal skin in the adult are already apparent in large pouch young.

PHYSIOLOGY.

From the morphological findings one may conclude that the sternal colour patch represents a male character which has its homologue in the female though on a lesser scale. This assumption is supported by the following observations.

With the approach of sexual maturity the brown colour patch on the sternum becomes very obvious in the male. An oily fluid in noticeable amounts appears to be secreted on the sternal region which, particularly during the breeding season, may be actually wet from this secretion. In captivity these males have been observed to rub the sternal region against protruding parts of the wall of the enclosure, and as a result a brown pigment is deposited in such places. Females, in which the development of the sternal patch is slower and less marked, have not so far been observed doing this. In fact in this sex the sternal hairs appear to be almost dry during the breeding season. However, increased secretory activity, as indicated by the wetness of the sternal region and the staining of surrounding hairs, is noted in the mother two or three months after a young possum is born; and the young, after leaving the pouch, have frequently been seen licking the sternal area of the mother.

In order to obtain some information on the nature of the sternal secretion pilocarpine was administered to male and female possums. The administration of 0.1-0.2 grain of pilocarpine, in all animals injected caused profuse sweating on the soles of the feet, and small beads of sweat were also seen on the clipped sternal area in both sexes, but to a greater degree in males than in females. The secretions throughout were alkaline in reaction. In all cases the fluid, which was collected by blotting with filter paper, was colourless in daylight. Fluid from the sternal region of the male turned to yellow and then to reddish-

brown within a few days of exposure to air on the filter paper. In the female this change was less marked but samples of sweat containing considerable amounts of this or a similar chromogen were obtained from the pouch. Sweat from the foot pads of both males and females contained very little or no chromogen. However, judging from experiments in which hair or skin or both have been extracted with ether and water in the soxhlet apparatus for a considerable time it may be concluded that the chromogen, though in much smaller amounts, is secreted by the skin in general, though here, too, more markedly in the male than in the female. From experiments with male sex hormones, which will be reported in detail on another occasion, there is further supporting evidence that in the male the sternal region undoubtedly is the preferential site for the excretion of the chromogen but that smaller amounts are secreted by the skin in general. It may be of interest to recall that Bolliger and Whitten (1940) reported the appearance of a chromogen in the urine of male and female *Trichosurus vulpecula* which on standing in an alkaline medium produced a brown colour; it seems possible that these two substances, the one from the skin and the other from the urine, are similar.

If the hairs of the sternal patch as well as some of those surrounding it which may also be stained brown, are cut off, the new hairs regenerating will be brown again if they belong to the typical sternal area, while the hairs surrounding the sternal region and belonging to the integument in general will appear as white hairs and remain so until stained again from secretions derived from the specific sternal skin.

Compared with the rest of the fur, the sternal hairs show only little fluorescence when examined with ultra-violet light in a darkened room, and practically none when covered with skin secretion (Bolliger, 1944).

DISCUSSION.

So far only scant attention has been given in the literature to the distinctively coloured patch of fur over the sternal area of *Trichosurus vulpecula*. Le Souef and Burrell (1926) and Troughton (1941) in their recent books on the animals of Australia do not mention it. Wood-Jones (1924) in his description of the bushy-tailed possum (*Trichosurus vulpecula*) as occurring in southern Australia states that on the ventral aspect the hairs are of a dirty white colour with a slight yellowish red tinge. "This yellowish colour is accentuated on the chest in the males and around the pouch in the females." Bolliger and Carrodus (1938) mentioned that in young females a brown streak over the sternum may or may not occur. From observations on over 100 individual possums from eastern N.S.W., it may now be stated that in fully grown sexually mature animals a brown sternal streak is always present, though varying considerably in size and being much more prominent in males.

In comparing the brown sternal area with the yellow-orange or brown hairs present in the pouch of females, it may be said that the latter is a female character while the former may be considered a rudimentary male character when occurring in females. The orange or brown hairs which frequently surround the opening of the pouch simply represent temporarily stained abdominal hairs and cannot be compared with the straighter and sparser sternal hairs which are permanently stained through the whole fibre from the follicle papilla to the tip, and which are different from the remaining pelage of the possum.

The pelage has few outstanding features to distinguish it from that of other mammals in various families possessing a dense woolly coat.

The integument, in its histological structure, is fairly typical of the marsupials so far examined. All the sweat glands present in the furry skin are of the apocrine type only. The skin of the sternal region differs from the rest of the integument



Fig. 3.



Fig. 2.

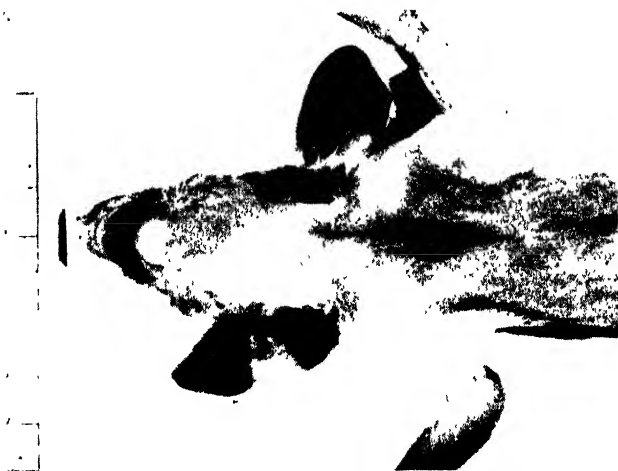


Fig. 1

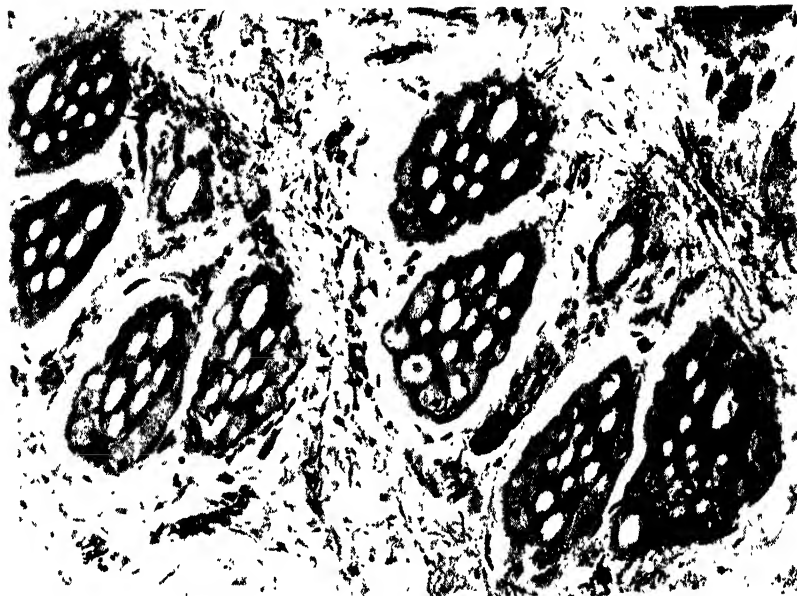


Fig. 4.



Fig. 5.

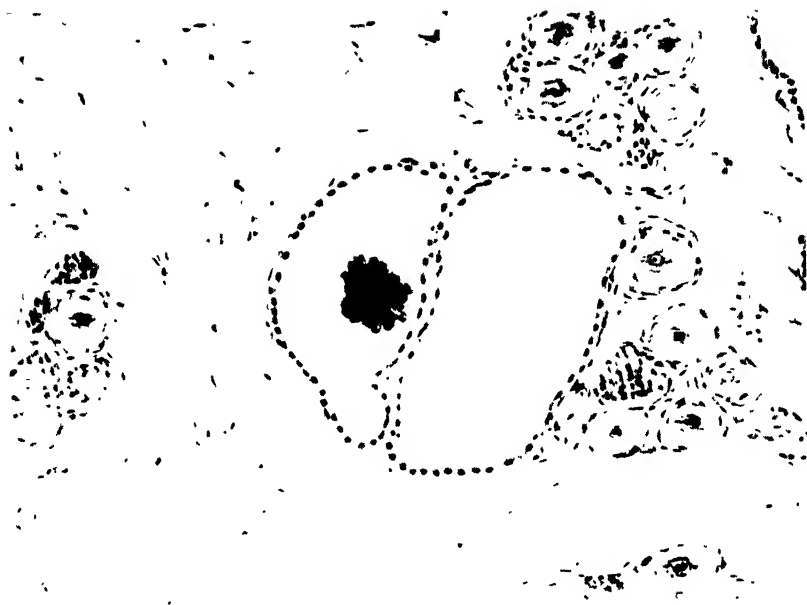


Fig. 6.



Fig. 7.



Fig. 8.



Fig. 9.



Fig. 10.

only in the degree of development of various structures. There seems to be no justification for the term "sternal gland" as it has been applied in other animals, and which implies something structurally discrete. The region is merely a limited but diffuse area of skin where certain structures such as the sebaceous and sudoriferous glands found normally over the general integument are locally enhanced in size and activity.

In the fully grown male the sternal area attracts immediate attention due to the rich colouring and shiny "lacquered" appearance of the sternal hairs. As has been shown, this is due to a copious local skin secretion containing a chromogen which, within a few days, is converted into an orange-brown pigment, heightening the colouring of the sternal hairs proper and temporarily staining the surrounding hairs. In the normal female all these manifestations are on a smaller scale and more confined to the region of the pouch, and this may explain why well-formed and fairly large crystals, tentatively considered to be urates, were only found in the sternal sweat glands of the male.

The biological significance of the sternal region is very probably that of an organ attracting the other sex by its colour and by the odour of its copious secretion. In the male both functions become very noticeable when approaching sexual maturity. These functions may also be employed by the male to mark a tree or a building which it inhabits in order to guide the prospective partner, an expedient probably necessary for nocturnal animals living widely dispersed. Similar behaviour, such as marking trees, has been noticed in the male of the koala (*Phascolarctos cinereus*). The odour, and probably the stain, from the sternal region of the mother may assist the young to find its parent after it has left the pouch, because in this period the female sternal secretion seems to be at its maximum.

A sternal area characterised by large and active glands, as well as vividly coloured hairs, has so far only been met with in *Trichosurus vulpecula*. However, Beddard (1887) described an almost hairless glandular patch "just anterior to the sternum" in another marsupial, the banded ant-eater (*Myrmecobius fasciatus*). This was confirmed by Bourne (1934) and Ford (1934) and the latter referred to the frequent occurrence of sternal or pectoral glands in marsupials, however, without giving any specific instances besides *Myrmecobius*. On superficial examination, no such sternal areas could be observed in the bandicoot (*Perameles nasuta*), grey kangaroo (*Macropus major*) or one species of wallaby, but the male of the native bear (*Phascolarctos cinereus*) seems to possess such an area, rich in active skin glands (MacKenzie, 1934). Bourne (1934) described glandular gular areas or pouches in some Australian Jerboa mice (*Notomys cervinus*, *Notomys mitchelli* and *Podanomalus* sp.) which probably are of a similar nature as those found in marsupials. He also observed a gular pouch in a bat (*Nyctinomus australis*). Amongst other mammals, sternal areas characterised by marked glandular secretion were described in primates such as the orang-utang (*Simia* sp.) (Wislocki and Schultz, 1925) and the spider monkey (*Ateles* sp.) (Schwarz, 1937). In all these mammals, including *Trichosurus vulpecula*, the same anatomical features appear to be present, i.e. an enlargement of the sebaceous and sudoriferous glands in a small area in the neighbourhood of the sternum. In *Trichosurus vulpecula* the connection between this accumulation of glands and the sex life of the animal seems fairly well established.

SUMMARY.

On studying the skin and hairs of *Trichosurus vulpecula* in pouch young and in fully grown specimens, it was found that at the age of three months a pigmented area appeared over the sternal region which subsequently developed into the distinctive sternal area.

The morphology of the skin over the sternum was similar to that of the rest of the body but there were differences in the relative size and activity of several structures. The most important difference noted was that in the sternal area both sebaceous and sudoriferous glands were very large and active. For example, in one specimen sebaceous glands on the sternum had about 15 times the volume of those on the dorsum, and sudoriferous glands had about 25 times the volume of those on the back. The skin secretions were found to be as copious as the size of the glands suggested, giving the hairs, particularly in the male, a wet and oily appearance. In addition, the secretion contained a chromogen which stained the sternal hairs, as well as the surrounding hairs, a vivid brown.

The hairs on the sternal area of the fully grown animal were notable for their distinctive brown coloration, which was present throughout the shaft, and for their straightness and sparseness.

These hairs may be considered to be a secondary sex character. They cover a larger area and are more brilliant in the male than in the female. The associated skin glands also were apparently more actively secreting in the male than in the female, and well formed crystals believed to be urates were found in the lumen of the sweat glands of the male only.

ACKNOWLEDGMENTS.

We wish to thank Mr. H. B. Carter for his encouragement and valuable criticism. We are indebted to Mr. E. Parrish for the microphotography, Mr. S. Woodward Smith for the macrophotography, and Mr. W. Clarke for the histological preparations. We also wish to thank the Council for Scientific and Industrial Research, and particularly Mr. D. A. Gill, Officer-in-charge, for accommodation given to one of us (M.H.H.) at the McMaster Laboratory.

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EXPLANATION OF PLATES.

PLATE IV.

Fig. 1.—Sternal area in male pouch young of about $3\frac{1}{2}$ months of age. Note the grey hairs over this area.

Fig. 2.—Sternal area of fully grown female, *Trichosurus vulpecula*.

Fig. 3.—Sternal area of a fully grown male. Note the characteristic lateral expansion of the deeply coloured sternal hairs.

PLATE V.

Fig. 4.—Dorsal skin region of male adult possum. Section cut parallel to the skin surface and showing two groups of hair follicles. Note the sebaceous tissue surrounding each lateral cluster of follicles, and the two sudoriferous ducts, linked to the central follicles by connective tissue traversing the middle of the group. The fibres are not pigmented. $\times 150$.

Fig. 5.—Sternal skin region of male adult possum. Section cut parallel to the skin surface and showing one follicle group. Compare with Fig. 4 and note the large and actively secreting sebaceous glands, the large sudoriferous duct, and the small number of fibres, most of which are pigmented. $\times 150$.

PLATE VI.

Fig. 6.—Sternal skin region of male adult possum at the level of the sudoriferous glands. Section cut parallel to skin surface and showing two portions of the secretory tube of a sudoriferous gland lying beside a group of hair follicles. The secretory epithelium varies in height on different parts of the gland wall, and a mass of crystalline material is seen in the lumen. $\times 150$.

Fig. 7.—Section through the secretory portion of a sudoriferous gland in the sternal region of an adult female possum. Note the high secretory epithelium with processes projecting into the lumen, and the granular secretory material within the lumen. $\times 150$.

PLATE VII.

Fig. 8.—Crystals in the lumen of a sudoriferous gland in the sternal region of an adult male possum. Section cut parallel to skin surface. The rosette of rod-shaped crystals is in the lumen of the secretory portion of a sudoriferous gland. At the upper right the transition from the secretory portion of the gland to the duct is seen. In the upper left a pigmented hair fibre is cut obliquely. $\times 500$.

Fig. 9.—Crystals in the duct of a sudoriferous gland in the sternal region of an adult male possum. Section cut parallel to skin surface. Note the layers of cells forming the wall of the duct, and the two clumps of crystals in the lumen. Above is part of a sebaceous gland, and to the left is portion of a hair follicle. $\times 500$.

Fig. 10.—Crystals in the wall of a sudoriferous gland in the sternal region of an adult male possum. Section cut parallel to skin surface. Note the crystalline rods mainly in the connective tissue sheath of the gland, and the blood capillary in the lower centre of the photograph. $\times 500$.

STUDIES IN THE PHENANTHRIDINE SERIES.

PART I. THE CYCLISATION OF 2-FORMAMIDO-DIPHENYLS.

By E. RITCHIE, M.Sc.

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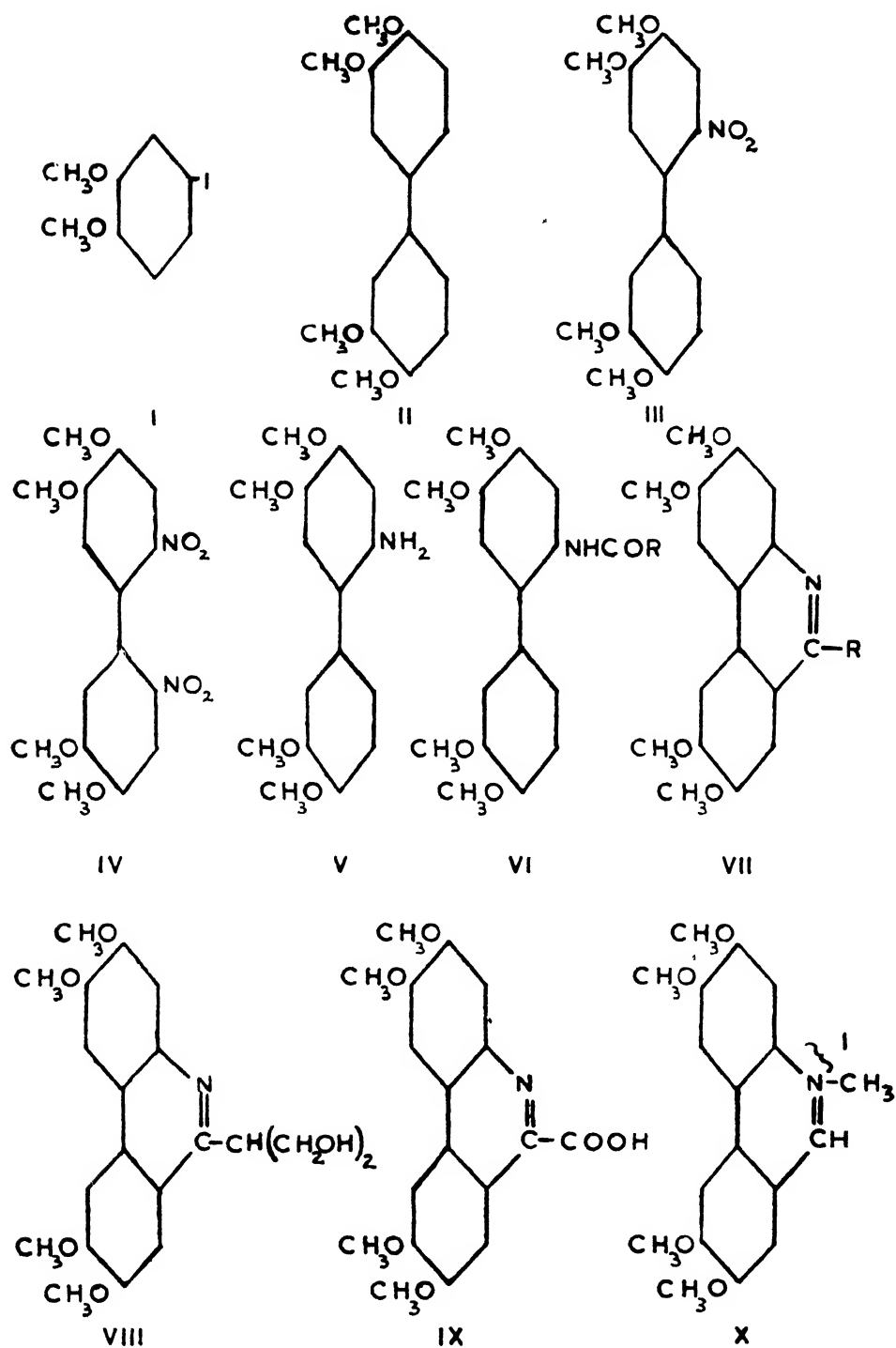
The chemistry of phenanthridine has probably been studied less than that of any of the simple ring systems. The lack of interest in the past was due no doubt to the comparative inaccessibility of phenanthridine derivatives and to the fact that no natural products derived from phenanthridine were known. In recent years, however, interest in this series has been stimulated by the discovery that the lycorine and the chelidonine-sanguinarine alkaloids are derivatives of phenanthridine and by the possibility of obtaining therapeutic agents.

A number of phenanthridine syntheses are known, but most of them use high temperatures or other drastic conditions, which greatly restricts their usefulness. The most attractive synthesis is that of Morgan and Walls, who found that the acyl derivatives of 2-amino-diphenyls are cyclised to phenanthridines by boiling with phosphorus oxychloride. These starting materials have lately been rendered much more accessible by improvements effected in the Gomberg reaction and by the commercial availability of certain diphenyl derivatives.

Apart from the publications of Morgan and Walls there is no information in the literature on the scope and applicability of this reaction or on its mechanism. Certain aspects of these questions have been studied in the work which follows, in the description of which all ring systems are named and numbered according to "The Ring Index" (A. M. Patterson and L. T. Capell, 1940, the Reinhold Publishing Corporation, New York). Ring Index numbers (R.I. No.) are also quoted for the less common systems.

By fusion with anhydrous zinc chloride at 250–300°, Pictet and Hubert (1896) cyclised acyl-o-amino-diphenyls to the corresponding phenanthridines. Because of the high temperature used, extensive charring occurred, purification was tedious and wasteful, and the yields were low. Moreover the reaction could not be applied to substances containing reactive groups such as nitroxyl. Later Morgan and Walls (1931) found that these defects were largely eliminated by using boiling phosphorus oxychloride to effect the cyclisation, and now this reaction is the most generally useful method for the synthesis of phenanthridines.

Although 2-formamido-diphenyl is converted by zinc chloride to phenanthridine, the cyclisation cannot be accomplished by phosphorus oxychloride. This unexpected result is unfortunate, because it would appear to render phenanthridines unsubstituted in the 6 position not directly accessible by this reaction. In the well-known Bischler-Napieralski reaction, which is very similar to the Morgan-Walls reaction, formyl- β -phenylethylamine gives a small yield of dihydro-isoquinoline (Decker, Kropp, Hoyer and Becker, 1913) and Bamberger and Goldschmidt (1894) also found that isoquinoline was obtained in low yield by the action of phosphorus pentoxide on cinnamaloxime, which presumably first underwent a Beckmann transformation to ω -formamido-



styrene. However, when a strongly para directing group is para to the position of ring closure, cyclisation occurs easily (Callow, Gulland and Haworth, 1929) and dihydro-isoquinolines are obtained in good yields from such substituted β -phenylethylamines (e.g. Richardson, Robinson and Seijo, 1937). In this connection para methoxyl and 3 : 4 dimethoxyl are particularly effective.

This suggested that it would be of interest to apply the Morgan-Walls reaction to a 2-formamido-diphenyl appropriately substituted by such an activating group, since it could be safely concluded that if cyclisation did not occur or if a low yield were obtained, then cyclisation would not take place to any useful extent in other cases.

A substance suitable for this purpose was synthesised through the intermediates shown in the chart. 4-Iodo-veratrole (I), which was readily obtained by a modification of the method of Seer and Karl (1913), was converted to 3 : 3' : 4 : 4'-tetramethoxy-diphenyl (II) by heating with copper powder (Späth and Gibian, 1930). When nitrated under mild conditions, this yielded a mono-nitro compound (III), the constitution of which was proved by further nitration to the known 2 : 2'-dinitro-4 : 4' : 5 : 5'-tetra-methoxy-diphenyl (IV) (Hughes, Lions, Maunsell and Wright, 1937). This substance was also directly obtainable by dinitration. By catalytic reduction of the mono-nitro compound using Raney nickel, an almost quantitative yield of the corresponding amine (V) was obtained, which was readily characterised by its piperonylidene and salicylidene derivatives.

The formyl, acetyl, propionyl and benzoyl derivatives of the base (VI, $R_1=H$, $R_2=CH_3$, $R_3=C_2H_5$, $R_4=C_6H_5$, respectively) were prepared by the usual methods and then subjected to the action of boiling phosphorus oxychloride. As anticipated, the three latter substances were rapidly and almost quantitatively cyclised to the corresponding phenanthridines (VII, $R_2=CH_3$, $R_3=C_2H_5$, $R_4=C_6H_5$, respectively). The formyl derivative, however, was converted to an intractable tar and a similar result was obtained when the reaction was carried out in boiling toluene. At lower temperatures either a tar formed or there was no reaction. When the cyclisation was attempted by phosphorus pentoxide in boiling xylene the results were more hopeful and there was eventually obtained a product from which a pure crystalline methiodide could be isolated in very low yield. This substance analysed correctly for a tetramethoxy-phenanthridine methiodide and behaved as expected, but to establish its identity with certainty it was essential to make a direct comparison with an authentic specimen.

The synthesis of the required 2 : 3 : 8 : 9-tetramethoxy-phenanthridine methiodide was achieved by the degradation method of Walls (1934). By condensation with formaldehyde, the methyl-tetramethoxy-phenanthridine (VII, $R_2=CH_3$) yielded 6-($\beta\beta'$ -dihydroxy-isopropyl)-2 : 3 : 8 : 9-tetramethoxy-phenanthridine (VIII), which on oxidation afforded the carboxylic acid (IX). On heating, this decarboxylated smoothly to 2 : 3 : 8 : 9-tetramethoxy-phenanthridine (VII, $R_1=H$), which readily formed a methiodide (X). This substance proved to be identical with that obtained from the cyclisation of the formyl derivative (VI, $R_1=H$). Hence it must be concluded that even in the most favourable case ring closure occurs to a very small extent only and the cyclisation of 2-formamido-diphenyls is not a reaction of preparative value.

The phenanthridine derivatives prepared above are all colourless crystalline substances which show a marked blue fluorescence in neutral solution. In glacial acetic acid the fluorescence is stronger, but the yellow salts with mineral acids are too insoluble in water or alcohol to show this phenomenon. However, the yellow methiodides are strongly fluorescent in aqueous-alcoholic solution.

EXPERIMENTAL.

4-Iodoveratrole (I).

A solution of veratrole (56 g.) in alcohol (150 c.c.) was vigorously stirred and treated alternately with iodine (100 g.) and mercuric oxide (60 g.) during three hours. After another hour the reaction mixture was filtered and the alcohol distilled from the filtrate. The residue was dissolved in ether and the ethereal solution washed successively with sodium thiosulphate solution, dilute sodium hydroxide solution and water. After drying, the ether was removed and the residue distilled under reduced pressure. The product (60 g.) boiled at $163-4^{\circ}/26$ mm. The forerun (21 g.) consisting of veratrole and iodoveratrole, was suitable for another batch.

3 : 3' : 4 : 4'-Tetramethoxy-diphenyl (II).

The method of Späth and Gibian was modified as follows: A mixture of 4-iodoveratrole (25 g.) and copper powder ("Naturkupper C", 25 g.) was heated in a stream of carbon dioxide, with intermittent stirring, in an oil bath. When the temperature of the bath reached about 235° a vigorous reaction set in. Heating was interrupted until this had abated and then continued for an hour longer. After cooling, the reaction mixture was powdered and extracted with methyl alcohol. Evaporation of the extract to a small bulk yielded the nearly pure product (10 g.), which, recrystallised from the same solvent, had m.p. 133° , as reported by Späth and Gibian.

2-Nitro-4 : 4' : 5 : 5'-tetramethoxy-diphenyl (III).

A solution of tetramethoxydiphenyl (5.5 g.) in glacial acetic acid (60 c.c.) at room temperature was stirred and treated with nitric acid (1.2 c.c., sp. gr. 1.4) in glacial acetic acid (3 c.c.) during fifteen minutes. After an additional thirty minutes, the reaction mixture was warmed on the water bath for fifteen minutes, cooled and diluted with ice water. The precipitate was collected, washed, dried and recrystallised from alcohol from which it (5 g.) separated as yellow rhombs, m.p. 149° .

Found: C, 60.1; H, 5.2; N, 4.6%. Calculated for $C_{16}H_{17}O_6N$: C, 60.2; H, 5.3; N, 4.4%.

2 : 2'-Dinitro-4 : 4' : 5 : 5'-tetramethoxy-diphenyl (IV).

This substance was prepared from both tetramethoxydiphenyl and nitro-tetramethoxy-diphenyl by the same method. A solution (1.5 g.) in glacial acetic acid (15 c.c.) was treated with nitric acid (1.5 c.c., sp. gr. 1.4) at room temperature. The product soon began to crystallise. After ten minutes, water was added and the product collected. It crystallised from alcohol in fine yellow needles, m.p. 218° , identical with an authentic specimen (Hughes *et al.*, *loc. cit.*).

2-Amino-4 : 4' : 5 : 5'-tetramethoxy-diphenyl (V).

When a solution of the mono-nitro compound (III, 5 g.) in hot alcohol (200 c.c.) was shaken at normal pressure in an atmosphere of hydrogen in the presence of Raney nickel, slightly more than the theoretical amount of hydrogen was absorbed. After filtering off the catalyst, the alcohol was removed and the residue crystallised from benzene, from which it separated in nearly theoretical yield as colourless prisms melting at 151° .

Found: C, 66.6; H, 6.8%. Calculated for $C_{16}H_{19}O_4N$: C, 66.4; H, 6.6%.

The *piperonylidene* derivative prepared in alcohol from the base and piperonal as usual, separated from this solvent as yellow plates, m.p. 155° .

Found: C, 68.3; H, 5.9%. Calculated for $C_{24}H_{23}O_6N$: C, 68.4; H, 5.7%.

The *salicylidene* derivative formed orange needles from alcohol, m.p. 144° .

Found: C, 69.9; H, 5.8%. Calculated for $C_{23}H_{23}O_5N$: C, 70.2; H, 6.0%.

2-Acetamido-4 : 4' : 5 : 5'-tetramethoxy-diphenyl (VI, $R_2=CH_3$).

The base was readily acetylated by warming on the water bath for a short time with excess acetic anhydride. The product crystallised from aqueous alcohol as small colourless prismatic needles melting at 164° .

Found: C, 65.1; H, 6.2%. Calculated for $C_{18}H_{21}O_6N$: C, 65.3; H, 6.3%.

2-Propionamido-4 : 4' : 5 : 5'-tetramethoxy-diphenyl (VI, $R_1=C_2H_5$).

This substance, prepared in a similar fashion from propionic anhydride, separated from aqueous alcohol as small colourless plates, m.p. 138°.

Found: C, 65.7; H, 6.9%. Calculated for $C_{18}H_{18}O_4N$: C, 66.1; H, 6.6%.

2-Benzamido-4 : 4' : 5 : 5'-tetramethoxy-diphenyl (VI, $R_1=C_6H_5$).

A solution of the base (5.8 g.) in dry pyridine (10 c.c.) was treated with benzoyl chloride (2.8 g.) and heated on the water bath for one hour. After cooling, the reaction mixture was poured into dilute hydrochloric acid, and the product which soon solidified, collected, washed and recrystallised from aqueous alcohol. It separated in 85% yield as colourless glistening needles, m.p. 128°.

Found: C, 69.8; H, 6.0%. Calculated for $C_{23}H_{18}O_4N$: C, 70.2; H, 6.0%.

Cyclisation of the Amides (VI, $R_1=CH_3$, $R_2=C_2H_5$, $R_4=C_6H_5$).

The following procedure was used in each case: The amide (4 g.) was warmed with freshly distilled phosphorus oxychloride (10 c.c.) under reflux in a dry atmosphere. Almost immediately the solid turned bright yellow and clouds of hydrogen chloride were evolved. These soon diminished, but gentle refluxing was continued for one hour longer. Excess phosphorus oxychloride was removed under reduced pressure and the residue was then warmed with dilute sodium hydroxide solution. The liberated base was collected, washed, dried and recrystallised from benzene.

6-Methyl-2 : 3 : 8 : 9-tetramethoxy-phenanthridine (VII, $R_3=CH_3$).

This substance (85% yield) crystallised as colourless rods, m.p. 212°.

Found: C, 68.8; H, 6.3%. Calculated for $C_{18}H_{18}O_4N$: C, 69.0; H, 6.1%.

The *methiodide*, obtained by heating the base with excess methyl iodide in a sealed tube at 100° for two hours, separated from water to which a little alcohol had been added, in yellow needles, which begin to decompose at about 260° but do not melt completely until 284°.

Found: C, 49.8; H, 4.9%. Calculated for $C_{19}H_{20}O_4NI$: C, 50.1; H, 5.0%.

6-Ethyl-2 : 3 : 8 : 9-tetramethoxy-phenanthridine (VII, $R_3=C_2H_5$).

The pure compound (85% yield) formed colourless prisms melting at 202°.

Found: C, 69.9; H, 6.4%. Calculated for $C_{19}H_{20}O_4N$: C, 70.0%; H, 6.4%.

The *methiodide* prepared as above, crystallised from very dilute alcohol in yellow needles, melting and decomposing at 286°.

Found: C, 51.3; H, 5.2%. Calculated for $C_{20}H_{22}O_4NI$: C, 51.2; H, 5.1%.

6-Phenyl-2 : 3 : 8 : 9-tetramethoxy-phenanthridine (VII, $R_4=C_6H_5$).

The pure substance (90% yield) crystallised from benzene as small colourless blades, m.p. 207°.

Found: C, 74.0; H, 5.7%. Calculated for $C_{23}H_{18}O_4N$: C, 73.6; H, 5.6%.

The *methiodide*, prepared as usual, separated from dilute alcohol in yellow needles melting with decomposition at 273°.

Found: C, 55.7; H, 4.8%. Calculated for $C_{24}H_{20}O_4NI$: C, 55.7; H, 4.6%.

6-($\beta\beta'$ -dihydroxy-isopropyl)-2 : 3 : 8 : 9-tetramethoxy-phenanthridine (VIII).

A solution of methyl-tetramethoxy-phenanthridine (VII, $R_3=CH_3$; 10 g.) in alcohol (50 c.c.) and formalin (20 c.c. 40%) was refluxed for three hours and then more formalin (20 c.c.) added.

After heating for another ten hours an additional amount of formalin (10 c.c.) was added and refluxing continued for a further three hours. The syrup, obtained by evaporation, was taken up in water, made strongly ammoniacal, boiled and cooled. The solid which separated was collected, and recrystallised successively from benzene and benzene-alcohol (1 : 1) mixture. It (6.5 g.) separated as minute colourless prisms which melted at 214°.

Found : C, 64.5 ; H, 6.3%. Calculated for $C_{30}H_{28}O_6N$: C, 64.3 ; H, 6.2%.

2 : 3 : 8 : 9-Tetramethoxy-phenanthridine-6-carboxylic acid (IX).

A solution of the glycol (VIII, 4.5 g.) in water (50 c.c.) and concentrated sulphuric acid (1.2 c.c.) was heated on the water bath and stirred whilst it was treated during thirty minutes with a solution of potassium dichromate (7.5 g.) in water (35 c.c.) and concentrated sulphuric acid (5.6 c.c.). Oxidation proceeded gradually and after heating and stirring for an additional three hours, the reaction mixture was cooled and diluted. The crude acid which separated was purified by solution in hot dilute sodium hydroxide and reprecipitation by acetic acid. The colourless product (3.9 g.) then decomposed with evolution of carbon dioxide at about 240°. It was not purified further, but was used directly in the next step.

2 : 3 : 8 : 9-Tetramethoxy-phenanthridine (VIII, $R_1=H$).

When maintained at 245°, the acid was rapidly decarboxylated. The dark residue was taken up in alcohol, charcoaled, filtered and the sparingly soluble hydrochloride precipitated by the addition of a little concentrated hydrochloric acid. The regenerated base was extracted with hot benzene and the extract evaporated until crystallisation commenced. After cooling, the product (2.5 g.) was collected and recrystallised from methyl alcohol, separating as colourless needles which partially melted at 135°, resolidified and then melted at 185°. This behaviour is due to solvent of crystallisation, which is very tenaciously retained.

Found : C, 67.0 ; H, 6.0%. Calculated for $C_{17}H_{17}O_4N \cdot \frac{1}{2}(CH_3OH)$: C, 66.5 ; H, 6.0%.

The *methiodide* (X), prepared as usual, crystallised from aqueous alcohol in small pale yellow needles which darkened slightly at 265° and melted at 295°.

Found : C, 48.5 ; H, 4.4%. Calculated for $C_{18}H_{20}O_4NI$: C, 49.0 ; H, 4.5%.

2-Formamido-4 : 4' : 5 : 5'-tetramethoxy-diphenyl (VI, $R_1=H$).

A solution of the amine (V, 2 g.) in glacial formic acid (15 c.c.) was refluxed for three hours, then cooled and diluted. The precipitated product was recrystallised from aqueous alcohol from which it (1.7 g.) separated as small colourless diamond-shaped plates m.p. 168°.

Found : C, 64.2 ; H, 6.1%. Calculated for $C_{17}H_{19}O_5N$: C, 64.4 ; H, 6.1%.

Cyclisation of (VI, $R_1=H$).

A solution of the formyl derivative (7.5 g.) in dry xylene (80 c.c.) was refluxed for three hours with phosphorus pentoxide (10 g.) which gradually became yellow. After cooling a little, the xylene was decanted and the residue washed in turn with xylene and ether. The bases, liberated by the addition of dilute ammonia, were extracted with benzene and the extract evaporated to dryness. The residue was dissolved in alcohol and then treated with a little concentrated hydrochloric acid, which precipitated a mixture of sparingly soluble hydrochlorides. The regenerated bases, isolated with the aid of benzene, were methylated by heating with excess methyl iodide at 100° in a sealed tube for one hour. The product was washed with hot alcohol, then with hot water and finally recrystallised several times from aqueous alcohol, being much more soluble in this mixture than in either of its components. The substance (0.3 g.) thus obtained (X) formed small pale yellow needles, identical with that obtained above, as proved by identity of crystalline habits, solubilities, melting and mixed melting points.

Found : C, 48.6 ; H, 4.7%. Calculated for $C_{18}H_{20}O_4NI$: C, 49.0 ; H, 4.5%.

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STUDIES IN THE PHENANTHRIDINE SERIES.

PART II. THE CYCLISATION OF SOME 4'-BROMO AND 4'-DIMETHYLAMINO ACYL-2-AMINODIPHENYLS.

By E. RITCHIE, M.Sc.

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There is no information in the literature on the cyclisation of halogen substituted acyl- β -phenylethylamines to dihydro-iso-quinolines or on the influence of a heteronuclear halogen on the formation of phenanthridines from acyl-2-aminodiphenyls. From considerations of the inductive and resonance effects exerted by halogens it was anticipated that if the halogen was meta or para to the position of ring closure, then cyclisation would be rather more difficult than in an unsubstituted acyl-2-amino-diphenyl, but not so difficult as in the case of a meta nitro group (Morgan and Walls, 1932). The case when bromine is meta to the position of ring closure was examined in this work.

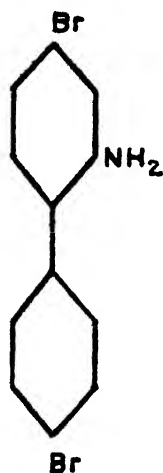
It has been shown (Morgan and Walls, 1932; Walls, 1935) that homonuclear substituents do not affect the ease of cyclisation, and consequently the acyl derivatives of the more readily accessible 2-amino-4 : 4'-dibromo-diphenyl (I) were studied rather than those 2-amino-4'-bromodiphenyl. The substance (I) was prepared by the bromination of diphenyl (Scholl and Neovius, 1911), followed by nitration to 2-nitro-4 : 4'-dibromo-diphenyl (Shaw and Turner, 1932) and reduction by stannous chloride in alcohol. The nitro compound was recovered unchanged when reduction by West's method (1925) was attempted. The acetyl (II, $R_1 = \text{CH}_3$) and benzoyl (II, $R_2 = \text{C}_6\text{H}_5$) derivatives were prepared by conventional methods.

When the acetyl derivative was boiled with phosphorus oxychloride the reaction was slow, as evidenced by the rate of evolution of hydrogen chloride, and extensive resinification occurred. However, from the reaction mixture 3 : 8-dibromo-6-methyl-phenanthridine (III, $R_1 = \text{CH}_3$) was isolated in about 7% yield, together with a neutral substance, not further studied in about 3% yield. When heated to 180° with phosphorus oxychloride in nitrobenzene solution, under the "forcing" conditions of Morgan and Walls (1939, 1940) resinification of (II, $R_1 = \text{CH}_3$) was rapid and complete. The benzoyl derivative, although cyclised slowly by boiling phosphorus oxychloride, was not resinified. After three hours, about 15% had cyclised and the remainder could be recovered. Under "forcing" conditions, however, cyclisation was complete in six hours and 3 : 8-dibromo-6-phenyl-phenanthridine (III, $R_2 = \text{C}_6\text{H}_5$) was obtained in nearly theoretical yield. The cyclisation in this case is effected in less than half the time (15 hours) required for 4'-nitro-2-benzamido-diphenyl under the same conditions. These results are in general agreement with the predictions made above.

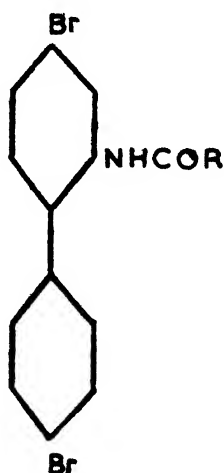
A similar study was made of the acetyl (V, $R_1 = \text{CH}_3$) and benzoyl (V, $R_2 = \text{C}_6\text{H}_5$) derivatives of 2-amino-tetramethyl-benzidine (IV). In these cases it was expected that cyclisation would be difficult to accomplish. These expectations were more than fulfilled, since all attempts to cyclise these substances produced uninviting tars from which no crystalline products could be isolated.

In the course of these experiments it was noticed that the acyl derivatives dissolved in pure nitrobenzene to deep red solutions, from which they could be

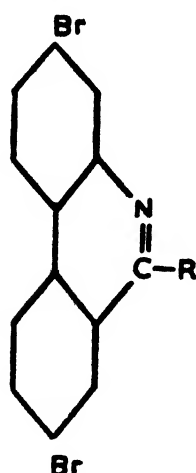
recovered unchanged. The same behaviour was shown by the parent base (IV), which was used for further experiments in this connection. It dissolved to a bright yellow solution in nitromethane, but in all other solvents examined, including acetonitrile and benzyl cyanide, no colour was observed. The



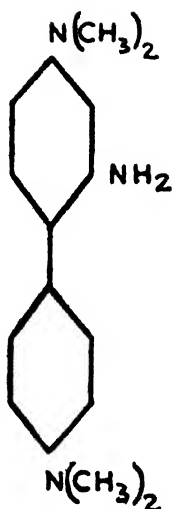
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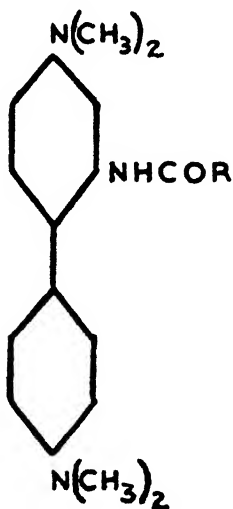
II



III



IV



V

phenomenon is not due to salt formation arising from traces of acids in the nitro compounds since the mineral acid salts of the base are colourless. The base readily formed a bright yellow picrate, and an addition compound with trinitro-toluene which crystallised from alcohol in beautiful black shining needles. The picrate is undoubtedly a true salt and the black substance a true molecular compound (Pfeiffer, 1927). All attempts to prepare addition compounds with o-, m- and p-nitro-toluenes and with m-dinitrobenzene were fruitless. According to Pfeiffer this is due to the formation in solution of coloured addition com-

pounds, which are too unstable to exist in the solid state, but later work by Gibson and Loeffler (1940) indicates that in these cases, postulation of unstable addition compounds is unnecessary and that the formation of coloured solutions should be attributed to the reciprocal polarisations of solvent and solute molecules.

The base (IV) condensed readily with salicylaldehyde to yield an orange Schiff's base, which dissolved in alcohol to an orange-yellow solution, but in nitrobenzene to a red solution. From *p*-dimethylamino-benzaldehyde there was obtained a yellow derivative which showed a similar behaviour in these solvents. However, the Schiff's bases derived from *o*-, *m*- and *p*-nitrobenzaldehydes and from 3- and 5-nitro salicylaldehydes were coloured deep red, brownish red, purple, brownish red and red respectively, and gave deep red solutions in both alcohol and nitrobenzene. These results, although not conclusive, would appear to support the conclusions of Gibson and Loeffler.

EXPERIMENTAL.

2-Nitro-4 : 4'-dibromo-diphenyl.

The crude product obtained by the method of Shaw and Turner (*loc. cit.*) was best purified by crystallisation from glacial acetic acid.

2-Amino-4 : 4'-dibromo-diphenyl (I).

A hot solution of the nitro compound (47 g.) in absolute alcohol (1,300 c.c.) was treated with a solution of stannous chloride (95 g.) in absolute alcohol (100 c.c.) and the mixture refluxed for twelve hours. After distilling off the alcohol the cooled residue was shaken with ether and dilute sodium hydroxide solution (1,000 c.c. of 10%). The ethereal extract was washed, dried and then the ether removed. The residue which crystallised spontaneously, was purified by recrystallisation from methanol yielding 27 g. Another recrystallisation from the same solvent gave the pure substance as colourless needles which melted at 132°.

Found : C, 44.3 ; H, 2.8%. Calculated for $C_{12}H_8NBr_2$: C, 44.0 ; H, 2.8%.

The substance was very sparingly soluble in light petroleum, moderately in methanol and easily soluble in other organic solvents.

2-Acetamido-4 : 4'-dibromo-diphenyl (II, $R_1=CH_3$).

Acetylation with acetic anhydride on the water bath in the usual manner afforded the acetyl derivative which crystallised from alcohol in colourless needles, m.p. 192°.

Found : C, 45.3 ; H, 3.0%. Calculated for $C_{14}H_{11}ONBr_2$: C, 45.5 ; H, 3.0%.

2-Benzamido-4 : 4'-dibromo-diphenyl (II, $R_1=C_6H_5$).

A solution of the amine (I, 9.8 g.) in dry pyridine (15 c.c.) was treated with benzoyl chloride (4.2 g.). After warming on the water bath for an hour in a loosely stoppered flask, the mixture was poured into dilute hydrochloric acid. On rubbing, the oil which separated was converted to a solid, which crystallised from alcohol as colourless needles (12 g.) which melted at 176°.

Found : C, 52.4 ; H, 3.1%. Calculated for $C_{18}H_{13}ONBr_2$: C, 52.9 ; H, 3.0%.

Cyclisation of the Acetyl Derivative (II, $R_1=CH_3$).

When a mixture of the acetyl derivative (7 g.) and phosphorus oxychloride (10 c.c.) was gently refluxed, hydrogen chloride was slowly evolved. After three hours this had almost ceased and the reaction mixture was dark reddish brown. It was cooled, basified with ammonia and extracted with benzene. After removing the benzene, the residue was dissolved in boiling alcohol (200 c.c.), charcoaled and filtered. On evaporation, the filtrate gradually deposited crystals *A*, which were collected from the hot solution when the volume had been reduced to about 30 c.c.

The hot filtrate was treated with alcoholic picric acid, and the crude picrate which separated on cooling and rubbing was collected and washed with alcohol. The regenerated base was taken up in benzene, and the solution washed, dried, and then evaporated to a small bulk. The crystalline mass which separated on cooling was collected, washed with a little benzene and recrystallised several times from ethyl acetate with the aid of charcoal. Eventually pure 3 : 8-dibromo-6-methyl-phenanthridine (III), ($R_1 = \text{CH}_3$; 0.5 g.) was obtained as small colourless needles which melted at 186° .

Found : C, 48.1; H, 2.6%. Calculated for $\text{C}_{16}\text{H}_9\text{NBr}_2$: C, 47.8; H, 2.5%.

The substance was easily soluble in benzene, less so in ethyl acetate, and only slightly in ethyl alcohol.

The *picrate* separated as small yellow needles when hot alcoholic solutions of its components were mixed. It decomposed at 235° .

Found : N, 9.9%. Calculated for $\text{C}_{20}\text{H}_{15}\text{O}_7\text{N}_4\text{Br}_2$: N, 9.7%.

The substance *A* after several recrystallisations from alcohol-benzene formed small colourless needles (0.2 g.), which melted and decomposed at 244° . Beyond noting that it was non-basic and did not form a *picrate*, it was not further examined.

3 : 8-Dibromo-6-phenyl-phenanthridine (III, $R_1 = \text{C}_6\text{H}_5$).

A mixture of the benzoyl derivative (II, $R_1 = \text{C}_6\text{H}_5$; 8 g.) nitrobenzene (20 c.c.) and phosphorus oxychloride (10 c.c.) was heated in an oil bath at 180° under reflux. After six hours the slow evolution of hydrogen chloride had ceased. The mixture was cooled, made strongly alkaline with dilute ammonia, and the nitrobenzene removed by steam distillation. The nearly pure product (7.5 g.) which had separated in light brown needles during the course of the steam distillation was collected and dried. Recrystallisation from benzene afforded the pure substance as long colourless needles which melted at 201° .

Found : C, 54.8; H, 2.7%. Calculated for $\text{C}_{21}\text{H}_{11}\text{NBr}_2$: C, 55.2; H, 2.7%.

It was fairly readily soluble in hot benzene, much less in cold benzene, and only slightly soluble in hot alcohol. Like (III, $R_1 = \text{CH}_3$), it formed a yellow insoluble salt with concentrated hydrochloric acid, which was completely hydrolysed by the addition of water.

The *picrate* prepared in alcohol-benzene solution, separated as bright yellow needles which melted at 223.4° with decomposition.

Found : N, 8.6%. Calculated for $\text{C}_{25}\text{H}_{14}\text{O}_7\text{N}_4\text{Br}_2$: N, 8.8%.

2-Nitro-tetramethyl-benzidine.

Tetramethyl-benzidine (Ullmann and Dieterle, 1904) was nitrated according to Bell and Kenyon (1926). The product crystallised from ethyl acetate containing a little benzene in beautiful deep red rhombs which melted at 165° (lit. 164°).

2-Amino-tetramethyl-benzidine (IV).

This substance was briefly described by Bell and Robinson (1927). The details of its preparation are as follows :

The powdered nitro compound (24 g.) was added during fifteen minutes to a stirred solution of stannous chloride (65 g.) in concentrated hydrochloric acid (100 c.c.), which had been warmed to 65° . It rapidly dissolved and the temperature rose to about 80° . The orange-red solution was then warmed on the water bath for fifteen minutes, cooled and poured into excess dilute sodium hydroxide solution. The precipitated product was extracted with benzene, the extract washed, dried and evaporated to a small bulk, when the nearly pure amine (20 g.) separated. One recrystallisation from alcohol yielded the pure substance as colourless needles which melted at 144° . Bell and Robinson (*loc. cit.*) report 138° .

Found : C, 74.9; H, 8.2%. Calculated for $\text{C}_{16}\text{H}_{11}\text{N}_2$: C, 75.3; H, 8.2%.

The *picrate* separated as sparingly soluble yellow needles when alcoholic solutions of its components were mixed. It began to darken at about 150° and decomposed at 167° .

Found : N, 17.1%. Calculated for $C_{23}H_{24}N_6O_7$: N, 17.3%.

The *trinitrotoluene addition compound* prepared in a similar fashion, crystallised as beautiful black shining needles, which began to melt at 87° , but were not completely liquefied until 112° .

Found : N, 17.5%. Calculated for $C_{23}H_{24}O_6N_6$: N, 17.4%.

2-Acetamido-tetramethyl-benzidine (V, $R_1=CH_3$).

The base (IV) was warmed on the water bath with excess acetic anhydride for five minutes and then poured into dilute ammonia. The product crystallised from aqueous alcohol in slender colourless needles, m.p. 157° .

Found : C, 72.4 ; H, 7.4%. Calculated for $C_{16}H_{23}ON_2$: C, 72.1 ; H, 7.7%.

2-Benzamido-tetramethyl-benzidine (V, $R_2=C_6H_5$).

Benzoylation with benzoyl chloride in pyridine solution was carried out as usual. The product crystallised from ethyl alcohol in faintly yellow prismatic needles which melted at 145° .

Found : N, 11.9%. Calculated for $C_{23}H_{25}ON_2$: N, 11.7%.

Condensation of the Base (IV) with Aldehydes.

The various Schiff's bases listed below were prepared from equimolecular proportions of the reactants in concentrated alcoholic solution as usual, and also recrystallised from alcohol.

Salicylidene-(2-amino-tetramethyl-benzidine).

Orange prisms, m.p. 119° . Alcoholic solution orange yellow, nitrobenzene solution red.

Found : C, 77.1 ; H, 7.3%. Calculated for $C_{23}H_{25}ON_2$: C, 77.3 ; H, 7.0%.

p-Dimethylamino-benzylidene-(base).

Yellow prisms, m.p. 140° . Alcoholic solution pale yellow, nitrobenzene solution red.

Found : C, 77.9 ; H, 7.7%. Calculated for $C_{25}H_{30}N_4$: C, 77.7 ; H, 7.8%.

o-Nitrobenzylidene-(base).

Small deep red needles, m.p. 175° . Alcoholic solution red, nitrobenzene solution red.

Found : C, 71.2 ; H, 6.2%. Calculated for $C_{23}H_{24}O_2N_4$: C, 71.1 ; H, 6.2%.

m-Nitrobenzylidene-(base).

Deep brownish red needles, m.p. 171° . Alcoholic solution red, nitrobenzene solution red.

Found : C, 71.3 ; H, 6.1%. Calculated for $C_{23}H_{24}O_2N_4$: C, 71.1 ; H, 6.2%.

p-Nitrobenzylidene-(base).

Purple needles, m.p. 212° . Alcoholic solution red, nitrobenzene solution red.

Found : C, 70.8 ; H, 6.3%. Calculated for $C_{23}H_{24}O_2N_4$: C, 71.1 ; H, 6.2%.

2-Hydroxy-3-nitro-benzylidene-(base).

Small brownish red prisms, m.p. 168° . Alcoholic solution red, nitrobenzene solution red.

Found : C, 68.2 ; H, 6.1%. Calculated for $C_{23}H_{24}O_3N_4$: C, 68.3 ; H, 6.0%.

2-Hydroxy-5-nitro-benzylidene-(base).

Red needles, m.p. 234° . Alcoholic solution red, nitrobenzene solution red.

Found : C, 68.1 ; H, 5.9%. Calculated for $C_{23}H_{24}O_3N_4$: C, 68.3 ; H, 6.0%.

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STUDIES IN THE PHENANTHRIDINE SERIES.

PART III. THE INFLUENCE OF THE ACYL GROUP IN THE MORGAN-WALLS REACTION AND THE MECHANISM OF THE REACTION.

By E. RITCHIE, M.Sc.

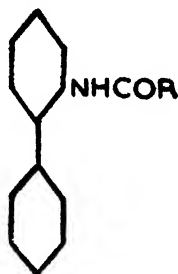
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The cyclisation of acyl derivatives of 2-amino-diphenyls by the Morgan-Walls reaction depends not only upon the presence and nature of nuclear substituents but also upon the nature of the acyl group. On the evidence available at the time relating to the latter effect, Walls (1934) summarised the position when he stated that "The course of the reaction must depend on the nature of R and of nuclear substituents, particularly in the heteronucleus. Although the reaction proceeds smoothly when $R=CH_2Cl$ it fails completely for $R=CHCl_2$ and CCl_3 , which suggests that as the negative character of R is increased, enolisation, the most probable preliminary to ring closure, is inhibited. The electronic character of R has however no consistent influence, for CH_2Cl gives better results than CH_3 but $COOC_2H_5$ gives a very poor yield and $CHCl_2$ fails; o- exceeds m- and p- $C_6H_4NO_2$ and equals C_6H_5 ." In order to gain additional information on this effect and with the hope of ultimately providing an adequate explanation for it, the cyclisation of a number of other acyl derivatives of 2-amino-diphenyl has been examined. At the outset it was realised that it would not be possible to examine the o-xenylamides of all types of acids and so it was decided to extend the investigations on some of those types already begun by Walls. The results of these experiments will be given first and a discussion of them will follow.

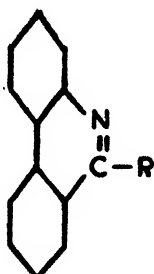
The observation that a poor yield was obtained when $R=COOC_2H_5$ led to the preparation and study of the o-xenylamides of the lower dicarboxylic acid half esters. A number of methods were employed to prepare the individual members of this series. The first member (I, $R=CH_2COOC_2H_5$) was obtained by refluxing the amine with excess malonic ester. On boiling with phosphorus oxychloride it was rapidly converted to a tar. The succinic acid derivative (I, $R=(CH_2)_2COOCH_3$) prepared by the action of β -carbomethoxy-propionyl chloride on the amine, was also resinified by the cyclising agent. The related acid (I, $R=(CH_2)_2COOH$), formed by mixing benzene solutions of succinic anhydride and the amine, gave a similar result. The third member of the series was synthesised in several steps. Glutaric anhydride and o-xenylamine reacted readily to form N-(o-xenyl)-glutaramic acid (I, $R=(CH_2)_3COOH$), which also failed to form a phenanthridine. On pyrolysis, this substance was dehydrated to N-(o-xenyl)-glutarimide (III) which was readily converted to 2-(γ -carbomethoxy-butylamido)-diphenyl (I, $R=(CH_2)_3COOCH_3$) by boiling with 1% sulphuric acid in anhydrous methyl alcohol. This substance was cyclised smoothly by phosphorus oxychloride, and the product, methyl γ -(6-phenanthridyl)-butyrate (II, $R=(CH_2)_3COOCH_3$) obtained in good yield. Hydrolysis by alcoholic potassium hydroxide in the usual manner afforded the corresponding acid. The last member of this series, which was examined (I, $R=(CH_2)_4COOC_2H_5$) was prepared from δ -carbomethoxy-valeryl chloride and o-xenylamine. This also was cyclised in good yield by phosphorus oxychloride

to the corresponding ethyl δ -(6-phenanthridyl)-valerate (II, $R = (CH_2)_4COOC_2H_5$), from which the related acid was obtained by the usual procedure.

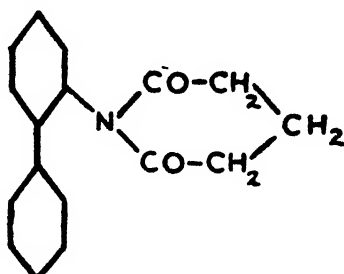
These results indicated that the study of the NN' di-o-xenylamides of the dicarboxylic acids would also yield interesting information. The study of this



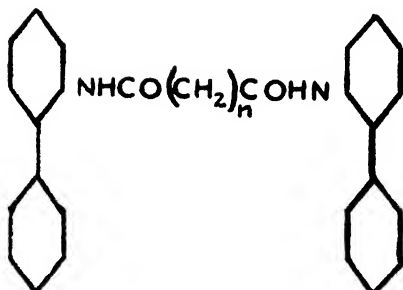
I



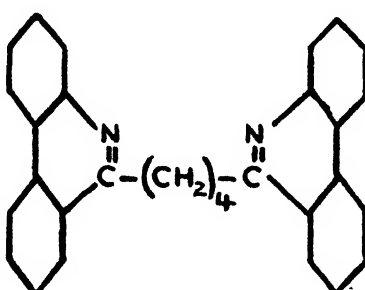
II



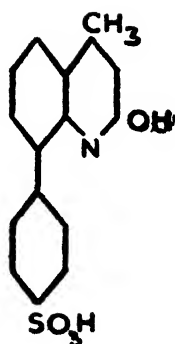
III



IV



V



VI.

series was begun in reverse order. Adipyl chloride and o-xenylamine gave a nearly theoretical yield of NN' di-o-xenyl-adipamide (IV, $n=4$), which gave two isomeric products on boiling with phosphorus oxychloride. The one formed in very small yield was weakly basic, fluoresced in acid solution, and formed a

picate. It is therefore regarded as 1:4-di-(6'-phenanthridyl)-butane (V). The other, a neutral substance obtained in nearly 50% yield, was not further investigated. The substituted glutaramide (IV, $n=3$), prepared from glutaryl chloride and *o*-xenylamine was slowly resinified by boiling with phosphorus oxychloride. After two hours approximately 50% of it was recoverable but no other product could be isolated. Further investigations in this series did not appear worth while.

The *o*-xenylamides of the third series examined were of the ω -phenyl-alkyl type, of which 2-benzamido-diphenyl may be regarded as the first member. The second member of the series (I, $R=CH_2C_6H_5$) was obtained as a low melting solid by the action of phenyl-acetyl chloride on *o*-xenylamine in dry pyridine. When boiled with the cyclising agent it was converted to 6-benzyl-phenanthridine (II, $R=CH_2C_6H_5$) in only 20% yield and no starting material could be recovered. A much better result was obtained from the next member of the series (I, $R=(CH_2)_2C_6H_5$), which also was prepared from the base and the corresponding acid chloride. In this case cyclisation proceeded smoothly and 6-(β -phenyl-ethyl)-phenanthridine (II, $R=(CH_2)_2C_6H_5$) was isolated in nearly 70% yield. An almost equally good result was obtained from the somewhat similarly constituted 2-(phenoxy-acetamido)-diphenyl (I, $R=CH_2OC_6H_5$), which gave 6-(phenoxy-methyl)-phenanthridine (II, $R=CH_2OC_6H_5$) in 65% yield.

It appeared to be of some importance to determine whether the principle of vinylogy (Fuson, 1935) held in this reaction. Accordingly 2-crotonamido-diphenyl (I, $R=CH=CHCH_3$), 2-cinnamamido-diphenyl (I, $R=CH=CHC_6H_5$) and *N*-(*o*-xenyl)-maleamic acid (I, $R=CH=CHCOOH$), the vinylogues of 2-acetamido-diphenyl, 2-benzamido-diphenyl and *o*-xenyloxamic acid, respectively, were prepared and then treated with phosphorus oxychloride. The first and last of these vinylogues were rapidly converted to tars from which no crystalline products could be isolated. But from the cyclisation of the second substance, 6-styryl-phenanthridine (II, $R=CH=CHC_6H_5$) was obtained in about 12% yield.

The cyclisation of 2-acetoacetamido-diphenyl (I, $R=CH_2COCH_3$), presented an interesting case since theoretically it could take place in two ways. Either 6-phenanthridyl-acetone could be formed by a Morgan-Walls reaction, or 2-hydroxy-4-methyl-8-phenyl-quinoline by a Knorr reaction. The amide was prepared in moderate yield by heating *o*-xenylamine with ethyl acetoacetate at 160° for a short time. When refluxed with phosphorus oxychloride it was rapidly converted to a tar, but cyclisation with concentrated sulphuric acid proceeded easily and cleanly. The product which was a sulphonic acid, gave no tests for a carbonyl group and therefore the cyclisation had taken the second course. It is probably 2-hydroxy-4-methyl-8-(phenyl-4'-sulphonic acid)-quinoline (VI).

One other aspect of the influence of the acyl group was examined. It seemed possible that cyclisation would be prevented or retarded if the acyl residue was bulky, and a few experiments were therefore carried out to ascertain if this steric factor was operative. It was found that 2-(α -naphthamido)-diphenyl was cyclised as rapidly as 2-benzamido-diphenyl (as far as could be judged from qualitative experiments) and the product 6-(α -naphthyl)-phenanthridine was isolated in 70% yield. In agreement with Pinck and Hilbert (1937), who had prepared it by another method, it was found to melt at 125°. This base also forms a methiodide without difficulty. It is noteworthy that the latter substance is dimorphous and both forms crystallise together from the same solution. On standing or more rapidly on rubbing, the yellow form changes to the stable orange form. The cyclisation of the mesitoyl derivative of *o*-xenylamine, which was very slowly formed when mesitoyl chloride (1 mol.) and *o*-xenylamine (2 mol.) were allowed to react in dry ether at room temperature, was then examined and found to proceed with equal facility. In this case also,

the reaction with methyl iodide did not appear to be hindered. It must be concluded then that the size of the acyl group is not an important factor in the Morgan-Walls reaction.

The yields given in the cyclisation experiments described above refer to the amount of product isolated in a reasonable state of purity (i.e. melting within 5° of the correct m.p.). In those cases where cyclisation is reported to have failed, it is unlikely that even very small yields would have escaped detection since the isolation of phenanthridine derivatives is usually facilitated by the slight solubility of their picrates and salts with mineral acids.

THE MECHANISM OF THE REACTION.

The suggestion by Walls (*loc. cit.*) that the first and in some cases critical step in the reaction is enolisation, raises the question of the structure of amides. Amides of the type under discussion are associated and according to recent work (reviewed by Hunter, 1941) this association is due to hydrogen bond resonance, the nitrogen atom of one molecule being united through a hydrogen atom to the oxygen atom of another molecule. An amide molecule then has neither an amide nor an imidol structure but may be regarded as a resonance hybrid of these two forms. The postulation of an enolisation step therefore appears to be unnecessary.

In the mechanism now proposed, the first step is the formation of a carbonium ion under the influence of the strong acid, phosphorus oxychloride. The carbonium ion has the general formula $[X-N=C-R]^+$ (where X represents o-xenyl) in which the carbon atom originally has a share in six electrons only. The formation of this ion possibly occurs through the substitution of a chloride ion or a phosphate ion for a hydroxyl ion, but like other carbonium ions it is probably never entirely free from the influence of the anion. In the next step the positive and hence electrophilic carbon atom attacks a carbon atom at the cyclisation position where the electron density is comparatively high. Simultaneously a proton is released and immediately attaches itself to the lone pair of electrons of the nitrogen atom, thus forming a phenanthridinium ion.

According to this mechanism, cyclisation will depend on at least three factors :

- (a) the formation of the carbonium ion,
- (b) the stability of the carbonium ion, and
- (c) the electron density at the heteronuclear ortho carbon atoms.

By a consideration of these three factors it should therefore be possible to account in a large measure for the experimental results.

The slight effect of a homonuclear substituent is readily understandable since it would affect (a) and (b) very slightly and (c) hardly at all. A heteronuclear substituent, on the other hand, largely controls the electron density at the position of ring closure by its inductive and resonance effects. If it increases the electron density at this point it should therefore facilitate cyclisation, but if it decreases it, cyclisation should be hindered. Experimentally this is found to be the case; for example, when a methoxyl group is para, the cyclisation proceeds very easily (Part I), but when a nitro group is meta, "forcing" conditions are required (Morgan and Walls, 1932, 1939, 1940). It should be noted that when there is no substituent in the heteronucleus, the electron density at the strategic carbon atom is still high, because it is ortho to an electron releasing group, i.e. the homonucleus.

Both the formation of the carbonium ion and its stability are affected by the nature of the acyl residue. If the carbonium ion cannot be formed, cyclisation cannot occur, and if the ion is formed very slowly, cyclisation is slow. In these cases the amide may be recovered unchanged or it may undergo side

reactions with the cyclising agent. Side reactions may also occur when the ion is easily formed but is unstable. The yield of phenanthridine then depends on the relative rates of cyclisation and side reaction, i.e. it is determined by the stability of the ion. But if ion formation is easy and if it is stable, then cyclisation should be the predominant reaction.

In the following brief discussions of the individual cases, the course of the reaction to be expected is given first and then the experimental results are stated. These of course are qualitative only.

1. $R=H$. The ion is formed but simultaneously loses a proton, the overall effect being a dehydration to an isonitrile, which then undergoes side reactions. No phenanthridine is formed (M. and W., 1931).

2. $R=CH_3$. The ion is readily formed and is stabilised by an electron drift from the donor methyl group. The same remarks apply to homologues. Good yields are obtained (M. and W., 1931).

3. $R=CH_2Cl$. The strongly electrophilic nature of the chlorine makes ion formation more difficult, but once formed it is stable. The reaction should be slower than in 2.

The yield actually obtained is slightly better than in 2 (M. and W., 1931), but this is probably not significant and may be due to greater ease of isolation of the product.

4. $R=CHCl_2$, CCl_3 . The accumulation of electrophilic chlorine atoms completely prevents ion formation and since the amides are stable, they should be recoverable.

The amides are recovered uncharged (W., 1934).

5. $R=COOC_2H_5$. This is similar to 4, but the carbethoxy group is not so strongly electrophilic. Ion formation is difficult and hence cyclisation is slow. A low yield is obtained but unchanged amide is recoverable (W., 1934).

6. $R=CH_2COOC_2H_5$. The ion is formed readily but is unstable, immediately losing a proton from the reactive methylene group. The overall effect is dehydration to the azomethine $X-N=C=CHCOOC_2H_5$, which is then resinified by the cyclising agent.

The amide is rapidly converted to a tar.

7. $R=(CH_2)_2COOCH_3$. The case is probably similar to 6.

The amide is resinified.

8. $R=(CH_2)_3COOCH_3$, $(CH_2)_4COOC_2H_5$. The inductive effect of the ester group is not important at the γ (or δ) carbon atom and the case is similar to 2.

Good yields are obtained.

9. $R=(CH_2)_2COOH$. Stable ions are not formed, but the carboxyl group is converted to $COCl$ with the consequent formation of chain polymers. Similar remarks apply to the higher homologue.

No phenanthridine is formed and no amide is recoverable.

10. $R=CH_2COCH_3$. This case is similar to 6.

The amide is converted to a tar.

11. $R=C_6H_5$. Ion formation is easy and the ion is stabilised by resonance with the benzene nucleus.

Good yields are obtained (M. and W., 1931).

12. $R=o-C_6H_4NO_2$. This strongly electrophilic group should render ion formation very difficult and hence retard cyclisation.

The good yield actually obtained (M. and W., 1931) may be due to a so-called "ortho effect" such as a high stabilisation of the carbonium ion by the positive carbon atom gaining a share of two of the electrons of a nitroxyl oxygen, which would in fact lie close to it.

13. $R=p-C_6H_4NO_2$. The strong electron withdrawing action of this group is undisturbed by any "ortho effect". Ion formation is therefore difficult, but the ion is stable.

Cyclisation is slow, but unchanged amide is recoverable (M. and W., 1931).

14. $R=m-C_6H_4NO_2$. The case is similar to 13, but since the group is not so electrophilic, ion formation is easier and cyclisation faster.

The yield is good but not as good as in 11 (M. and W., 1931).

15. $R=CH_2C_6H_5$. The case is similar to 6, but the ion is more stable. The yield should be small and no amide recoverable.

The yield is small and no amide is recoverable.

16. $R=(CH_2)_2C_6H_5$, $CH_2OC_6H_5$. Electron displacements are now slight and unimportant, hence the ion should be stable and cyclisation should be straightforward as in 2.

Good yields are obtained.

17. Diamides (IV, $n=3, 4$). Good yields would be expected in both cases.

The slow resinification of (IV, $n=3$) and the very poor yield obtained from (IV, $n=4$) cannot be accounted for.

18. $R=CH=CHCH_3$. Ion formation would be easy but since the ion would have a conjugated structure, the positive charge would not reside on any one carbon atom. Hence cyclisation would be very slow and polymerisation, a most probable side reaction, would predominate.

The amide is converted to a tar.

19. $R=CH=CHCOOH$. Ion formation would be difficult as in 5 and side reactions as in 9 would occur.

The amide is converted to a tar.

20. $R=CH=CHC_6H_5$. This case is similar to 18, but the ion is sufficiently stabilised by the benzene nucleus acting as an electron donor to allow the formation of a small yield of phenanthridine.

The yield is small and no amide is recoverable.

The mechanism suggested for the reaction thus accounts for the influence of homo- and heteronuclear substituents and the effects of most acyl groups can also be explained. It is realised, however, that only a study of the kinetics of the reaction can establish its mechanism with certainty.

The Morgan-Walls reaction has many features in common with other cyclodehydrations brought about by strong acids and leading to the formation of heterocyclic compounds, such as the Bischler-Napieralski reaction, and the Combes quinoline synthesis. If the mechanism proposed above is the correct one, it will probably apply in its essentials to these reactions also.

EXPERIMENTAL.

Ethyl N-(o-xenyl)-malonamate, (I, $R=CH_2COOC_2H_5$).

A solution of o-xenylamine (15 g.) in ethyl malonate (70 g.) was gently refluxed for eight hours, during which time alcohol was slowly evolved. After removing unchanged reactants by steam distillation, the oily residue was taken up in ether, washed with dilute acid, then water and dried. The thick light brown oil (20 g.) left after removing the ether could not be induced to solidify.

When warmed with phosphorus oxychloride, there was a copious evolution of hydrogen chloride and the reaction mixture rapidly darkened, but no crystalline substance could be isolated.

Methyl N-(o-xenyl)-succinamate, (I, $R=(CH_2)_2COOCH_3$).

A solution of o-xenylamine (26 g.) in dry ether (500 c.c.) was stirred and treated rapidly with a solution of β -carbomethoxy-propionyl chloride (11.5 g.) in dry ether (100 c.c.). The amine-hydrochloride soon began to separate and after thirty minutes it was collected and washed well

with ether. The combined filtrates were washed successively with water, dilute acid and water and then dried. Removal of the ether left a colourless oil (22 g.) which solidified completely on cooling. The substance was easily soluble in the usual organic solvents, but only slightly soluble in light petroleum, and was best recrystallized from ether light petroleum mixture, from which it separated as long colourless needles m.p. 73°.

Found: C, 72.0; H, 5.9%. Calculated for $C_{17}H_{17}O_3N$: C, 72.1; H, 6.0%.

The substance was rapidly resinified when boiled with phosphorus oxychloride.

N-(o-Xenyl)-succinamic Acid, (1, $R=(CH_2)_2COOH$).

Succinic anhydride (5 g.) dissolved in hot dry benzene (75 c.c.) was added in one lot to a solution of o-xenylamine (8.4 g.) in the same solvent (25 c.c.). The product began to crystallize almost immediately but refluxing was continued for one hour. After cooling it was collected and washed with benzene. The pure substance (12.4 g.) crystallised from aqueous alcohol in colourless needles melting at 126°.

Found: C, 71.2; H, 5.6%. Calculated for $C_{16}H_{15}O_4N$: C, 71.4; H, 5.6%.

Hydrogen chloride was evolved, when the substance was boiled with the cyclising agent, but no phenanthridine derivative could be isolated from the reaction mixture.

N-(o-Xenyl)-glutaramic Acid, (I, $R=(CH_2)_3COOH$).

A solution of glutaric anhydride (25 g.) in hot dry benzene (500 c.c.) was treated with a solution of o-xenylamine (37 g.) in the same solvent (100 c.c.) and the mixture boiled for one hour. On cooling, the product which had separated in nearly quantitative yield was collected, washed with benzene and recrystallised from ethyl acetate. It formed colourless needles which melted at 137°.

Found: C, 72.2; H, 6.0%. Calculated for $C_{17}H_{17}O_4N$: C, 72.1; H, 6.0%.

It was easily soluble in alcohol, but very slightly soluble in benzene. Boiling with phosphorus oxychloride converted it to a tar.

N-(o-Xenyl)-glutaramide (III).

The above acid (25 g.) was melted and then refluxed gently over a free flame for ten minutes. Water was evolved and a little of the acid sublimed. The dark gum obtained on cooling was readily rendered crystalline by rubbing with solvents. The product (15 g.) was finally obtained colourless by several recrystallisations from alcohol with the aid of charcoal. By rapid crystallisation small prisms are formed, but by slow crystallisation large irregular rectangular plates showing the hour glass structure are obtained. It melted at 158°.

Found: C, 76.2; H, 5.6%. Calculated for $C_{17}H_{15}O_2N$: C, 76.4; H, 5.6%.

The substance was easily soluble in benzene and in hot alcohol, but slightly soluble in cold alcohol.

Methyl N-(o-xenyl)-glutaramate, (I, $R=(CH_2)_3COOCH_3$).

A solution of the imide (III; 13 g.) in dry methyl alcohol (100 c.c.) containing concentrated sulphuric acid (0.8 g.; i.e. 1%) was refluxed for three hours. Then solid sodium carbonate slightly in excess of the theoretical amount required to neutralise the acid, was added and the mixture evaporated to a small bulk. After the addition of water, the product was extracted with ether, the extract washed thoroughly with dilute sodium carbonate solution and water and then dried. Removal of the ether left a residue (11 g.) which rapidly solidified. The pure substance obtained by recrystallisation from acetone light petroleum mixture formed long colourless needles melting at 85°.

Found: C, 72.1; H, 6.4%. Calculated for $C_{18}H_{19}O_4N$: C, 72.7; H, 6.4%.

It was easily soluble in the usual organic solvents excepting light petroleum.

Methyl γ -(6-phenanthridyl)-butyrate, (II, $R=(CH_2)_3COOCH_3$).

The above half-ester amide (6 g.) and boiling phosphorus oxychloride (12 c.c.) reacted vigorously. After refluxing gently for one hour, excess cyclising agent was distilled off under

reduced pressure, the residue dissolved in alcohol and the solution poured into excess dilute ammonia. The precipitated oil was extracted with ether, the solution dried, charcoaled, and evaporated. The residual oil solidified on rubbing and the solid obtained was recrystallised from light petroleum. The pure substance (3.6 g.) separated as colourless rods melting at 71°.

Found: C, 77.1; H, 6.0%. Calculated for $C_{18}H_{17}O_2N$: C, 77.4; H, 6.1%.

It was easily soluble in the usual organic solvents excepting light petroleum. Its solutions in glacial acetic acid and dilute sulphuric acid showed a blue fluorescence.

The *picrate* crystallised in sparingly soluble microscopic yellow plates, m.p. 198° with decomposition, when hot alcoholic solutions of its components were mixed.

Found: N, 11.1%. Calculated for $C_{24}H_{20}O_5N_4$: N, 11.0%.

γ-(6-Phenanthridyl)-butyric Acid, (II, R=(CH₂)₃COOH).

Hydrolysis of the above ester with alcoholic potassium hydroxide in the usual manner gave the acid. It crystallised from alcohol in rosettes of slender colourless needles melting at 158°.

Found: C, 76.7; H, 5.7%. Calculated for $C_{17}H_{15}O_2N$: C, 76.4; H, 5.6%.

Solutions of the substance in glacial acetic acid, dilute sulphuric acid, and in water show a blue fluorescence, but solutions in alcohol, benzene and dilute alkali do not. The fluorescence is obviously connected with phenanthridinium-salt formation, and this must occur also to some extent in aqueous solution.

Ethyl N-(o-xenyl)-adipamate, (I, R=(CH₂)₄COOC₂H₅).

This substance was prepared in dry ethereal solution from δ-carbethoxy-valeryl chloride (16 g.) and o-xenylamine (28.2 g.) by the usual method. It was isolated in nearly theoretical yield as a colourless syrup which could not be induced to crystallise.

Ethyl δ-(6-phenanthridyl)-valerate, (II, R=(CH₂)₄COOC₂H₅).

When the above half-ester amide (25 g.) was boiled with phosphorus oxychloride (35 c.c.) there was a vigorous evolution of hydrogen chloride. This soon diminished but refluxing was continued for one hour. Then excess phosphorus oxychloride was removed under reduced pressure, the residual gum dissolved in alcohol and the solution poured into excess dilute ammonia. The precipitated oil was shaken out with ether and after washing and drying, the ether was distilled off. The residue, which soon solidified, yielded the pure product (16 g.) after several recrystallisations from light petroleum. It formed long colourless needles which melted at 54°.

Found: C, 77.8; H, 6.7%. Calculated for $C_{20}H_{21}O_2N$: C, 78.2; H, 6.9%.

The *picrate* prepared in and recrystallised from alcohol separated as yellow needles m.p. 131°.

Found: N, 10.6%. Calculated for $C_{26}H_{24}O_5N_4$: N, 10.4%.

δ-(6-Phenanthridyl)-valeric Acid (II, R=(CH₂)₄COOH).

The acid, obtained by hydrolysis of the ester, crystallised from aqueous methyl alcohol in colourless needles. On heating it melted at 108°, but a clear melt was not obtained until 115°.

Found: C, 77.2; H, 6.3%. Calculated for $C_{18}H_{17}O_2N$: C, 77.4; H, 6.1%.

Solutions of this substance and of the related ester show the same fluorescence phenomena as those of their respective lower homologues.

N:N'-di-(o-xenyl)-adipamide, (IV, n=4).

When a stirred solution of o-xenylamine (33.8 g.) in dry ether (1,000 c.c.) was treated with a solution of adipyl chloride (9.2 g.) in ether (100 c.c.), precipitation of a white solid began almost immediately. After stirring for thirty minutes, this was collected and washed well with ether. The combined filtrates were washed with dilute acid and water and then dried. Evaporation of the ether left only a small amount of material and it was evident that the main bulk of the product remained with the amine-hydrochloride. This was extracted with hot benzene, and the extract evaporated to a small volume and then cooled, when the nearly pure product (21 g.)

separated. The pure substance crystallised from alcohol as colourless needles melting at 171° . It was fairly soluble in hot benzene, less so in hot alcohol, and sparingly in cold alcohol.

Found: C, 80.6; H, 6.0%. Calculated for $C_{30}H_{28}O_2N_2$: C, 80.4; H, 6.2%.

Cyclisation of (IV, $n=4$).

The diamide (19 g.) and phosphorus oxychloride (50 c.c.) were heated under reflux until evolution of hydrogen chloride had almost ceased (about two hours). After distilling off excess phosphorus oxychloride under reduced pressure, the dark residue was dissolved in hot alcohol and the resulting solution poured into excess dilute ammonia. The product was extracted with benzene, washed with water and dried over solid sodium hydroxide. The benzene solution was evaporated to a small bulk and then an equal volume of hot alcohol added. The substance *A* (7 g.) which separated on cooling was nearly pure.

The filtrate was taken to dryness and the residue dissolved in the minimum of hot ether. On standing a substance *B* (0.5 g.) separated. The filtrate from this was evaporated, the residue dissolved in the minimum of hot acetone and three volumes of alcohol added. After some time an additional amount of *A* (1.5 g.) crystallised out. From this last filtrate no crystalline product could be isolated.

The substance *B* crystallised from benzene in small elongated hexagons melting at 214° . It was sparingly soluble in the usual organic solvents. Its solutions in glacial acetic acid and in hot sulphuric acid showed a blue fluorescence, and its benzene solution gave an immediate precipitate with alcoholic picric acid. It is therefore regarded as 1:4-di-(6'-phenanthridyl)-butane (*V*).

Found: C, 87.0; H, 5.6%. Calculated for $C_{30}H_{24}N_2$: C, 87.4; H, 5.8%.

The substance *A* separated from alcohol benzene mixture in colourless needles, m.p. 167° . It is moderately soluble in hot benzene, but less so in alcohol.

Found: C, 87.1; H, 5.7%. Calculated for $C_{30}H_{24}N_2$: C, 78.4; H, 5.8%.

Solutions of the substance in glacial acetic acid and concentrated sulphuric acid were non-fluorescent. It did not form a picrate nor did it react with methyl sulphate in boiling toluene.

N : N'-di-(o-xenyl)-glutaramide, (IV, $n=3$).

The action of glutaryl chloride (9.8 g.) on o-xenylamine (39 g.) in dry benzene (700 c.c.) eventually yielded the crude diamide in over 90% yield. The pure substance crystallised from alcohol in long colourless needles melting at 162° .

Found: C, 80.4; H, 6.1%. Calculated for $C_{29}H_{26}O_2N_2$: C, 80.2; H, 6.0%.

The product of the reaction with boiling phosphorus oxychloride for two hours was a dark red gum from which only starting material (about 50%) could be isolated.

2-Phenylacetamido-diphenyl, (I, $R=CH_2C_6H_5$).

Phenylacetyl chloride (31 g.) and o-xenylamine (34 g.) reacted in dry pyridine (50 c.c.) to form the amide (55 g.). Purification of this was difficult but eventually by crystallisation from light petroleum containing a little ether it was obtained as a colourless wax-like solid m.p. 37° . It is easily soluble in the usual organic solvents.

Found: C, 83.2; H, 6.0%. Calculated for $C_{20}H_{17}ON$: C, 83.6; H, 5.9%.

6-Benzyl-phenanthridine, (II, $R=CH_2C_6H_5$).

The amide (45 g.) was gently refluxed with phosphorus oxychloride (100 c.c.) for one hour, during which time much hydrogen chloride was evolved and the reaction mixture darkened. After removing excess phosphorus oxychloride under reduced pressure, the residue was shaken with benzene and dilute ammonia. After washing and drying, the benzene solution was distilled, finally under reduced pressure. The fraction boiling at $270.5^{\circ}/18$ m.m. solidified on rubbing. Several recrystallisations from methyl alcohol afforded the pure product (8 g.) as colourless prismatic needles m.p. 112° .

Found: C, 88.8; H, 5.3%. Calculated for $C_{30}H_{15}N$: C, 89.2; H, 5.5%.

It was very easily soluble in benzene, but much less so in ethyl and methyl alcohols.

The *picrate* crystallised rapidly when hot alcoholic solutions of its components were mixed, as fine yellow needles. It sintered at about 190°, and then gradually decomposed.

Found: N, 11.4%. Calculated for $C_{21}H_{13}O_7N_4$: N, 11.2%.

2-(β -Phenyl-propionamido)-diphenyl, (I, $R=(CH_2)_3C_6H_5$).

This substance, prepared by the action of β -phenyl-propionyl chloride (11 g.) with o-xenylamine (22 g.) in dry ether (600 c.c.) in the usual manner, was purified by two recrystallisations from light petroleum containing a little acetone. It (15 g.) formed colourless needles m.p. 81°.

Found: C, 80.1; H, 6.2%. Calculated for $C_{21}H_{19}ON$: C, 80.4; H, 6.3%.

It was easily soluble in the usual organic solvents, excepting light petroleum.

6-(β -Phenyl-ethyl)-phenanthridine, (II, $R=(CH_2)_2C_6H_5$).

The above amide (14 g.) was cyclised by boiling with phosphorus oxychloride (25 c.c.) for one hour. The pure substance (9 g.) separated from methyl alcohol in colourless tablets which melted at 93°.

Found: C, 88.8; H, 6.0%. Calculated for $C_{21}H_{17}N$: C, 89.0; H, 6.0%.

The *picrate* prepared in alcohol crystallised in glistening yellow plates which began to decompose at about 170° but did not melt completely until 198°.

Found: N, 10.8%. Calculated for $C_{27}H_{20}O_7N_4$: N, 10.9%.

2-(Phenoxy-acetamido)-diphenyl, (I, $R=CH_2OC_6H_5$).

A solution of o-xenylamine (10 g.) in dry pyridine (20 c.c.) was treated with phenoxy-acetyl chloride (10 g.) and heated on the water bath for one hour. The material precipitated by pouring the reaction mixture into dilute hydrochloric acid soon solidified. By recrystallisation from methyl alcohol it was obtained in long colourless needles (15 g.) which melted at 91°. Frequently the needles were flattened and showed the hour glass structure.

Found: C, 79.4; H, 5.8%. Calculated for $C_{20}H_{17}O_2N$: C, 79.2; H, 5.6%.

6-(Phenoxy-methyl)-phenanthridine, (II, $R=CH_2OC_6H_5$).

When the amide (8 g.) was heated with phosphorus oxychloride (15 c.c.) it rapidly dissolved and hydrogen chloride was evolved. After one hour, the reaction mixture was cooled and poured into excess dilute ammonia. The product was extracted with benzene and the benzene solution washed and dried over solid sodium hydroxide. Evaporation of the benzene left an oil which easily solidified, but the product was contaminated with a small amount of amorphous material which could not be removed by recrystallisation. Purification was best effected by conversion to the *picrate* in alcoholic solution followed by regeneration. The substance (5 g.) then recrystallised from alcohol to which a little benzene had been added, in colourless needles m.p. 142°. It was easily soluble in benzene but less so in alcohol.

Found: C, 84.1; H, 5.5%. Calculated for $C_{20}H_{15}ON$: C, 84.2; H, 5.3%.

The sparingly soluble *picrate* separated from hot alcohol in small bright yellow needles which begin to decompose at about 170°.

Found: N, 11.1%. Calculated for $C_{21}H_{13}O_7N_4$: N, 10.9%.

2-Crotonamido-diphenyl, (I, $R=CH=CHCH_3$).

This substance was prepared in 90% yield from crotonyl chloride (1 mol.) and o-xenylamine (2 mol.) in dry ether in the usual manner. It crystallised from acetone light petroleum mixture in colourless needles which melted at 96°.

Found: C, 81.3; H, 6.2%. Calculated for $C_{18}H_{15}ON$: C, 81.0; H, 6.3%.

It was rapidly resinified by boiling phosphorus oxychloride.

2-Cinnamamido-diphenyl, (I, R=CH=CHC₆H₅).

The action of cinnamoyl chloride (15 g.) on o-xenylamine (15 g.) in dry pyridine (25 c.c.) in the usual manner yielded the cinnamoyl derivative. The pure substance (24 g.) separated from alcohol in fine colourless needles, m.p. 141°.

Found: C, 84.5; H, 5.9%. Calculated for C₂₁H₁₇ON: C, 84.3; H, 5.7%.

6-Styryl-phenanthridine, (II, R=CH=CHC₆H₅).

The above amide (8 g.) was refluxed gently with phosphorus oxychloride (15 c.c.), for one hour. Evolution of hydrogen chloride had then ceased and the reaction mixture was dark red. After cooling, it was poured into excess dilute ammonia and extracted with benzene. The benzene solution was evaporated to a small bulk and then treated with excess alcoholic picric acid. The picrate was collected and washed with warm alcohol and benzene. The base, regenerated in the usual manner, was nearly pure (0.8 g.). It crystallised from alcohol in long colourless slender needles melting at 133°. It was easily soluble in benzene, but less so in alcohol.

Found: C, 89.5; H, 5.4%. Calculated for C₂₁H₁₅N: C, 89.7; H, 5.3%.

The picrate crystallised from hot alcohol in very small bright yellow needles which decomposed at 237°.

Found: N, 11.1%. Calculated for C₂₇H₁₈O₇N₄: N, 11.0%.

N-(o-Xenyl)-maleamic Acid, (I, R=CH=CHCOOH).

When a solution of o-xenylamine (8.4 g.) in a little warm dry benzene was added to a solution of maleic anhydride (4.9 g.) in hot dry benzene, an orange colour developed. This rapidly faded to pale yellow and the product began to separate. After refluxing for thirty minutes, the reaction mixture was cooled and the nearly theoretical yield collected. The substance crystallised from alcohol in rosettes of small colourless needles m.p. 167°.

Found: C, 71.7; H, 4.9%. Calculated for C₁₆H₁₃O₃N: C, 71.9; H, 4.9%.

It is almost completely insoluble in hot benzene, but fairly soluble in hot alcohol. Attempts to cyclise it led to the formation of a dark green tar.

2-Acetoacetamido-diphenyl (I, R=CH₂COCH₃).

o-Xenylamine (10 g.) was melted and added in one lot to ethyl acetoacetate (40 g.) maintained at 160°. After ten minutes, when the brisk evolution of alcohol had ceased, the liquid was allowed to cool somewhat and the excess ester removed under reduced pressure. The oily residue solidified overnight and the material, after draining on a porous tile, was recrystallised from light petroleum containing a small amount of benzene. It separated as long colourless needles (9 g.) which melted at 84°.

Found: N, 5.6%. Calculated for C₁₈H₁₅O₃N: N, 5.5%.

When heated with phosphorus oxychloride, hydrogen chloride was evolved, but the product was a tar.

2-Hydroxy-4-methyl-8-(phenyl-4'-sulphonic acid)-quinoline (VI).

A solution of the amide (20 g.) in ice cold concentrated sulphuric acid (100 c.c.) was allowed to come to room temperature during thirty minutes and then heated on the water bath for twenty minutes. After cooling, the solution was poured into ice water (500 c.c.). The product (15 g.) which slowly separated was recrystallised from dilute sulphuric acid, forming colourless glistening leaflets, which did not melt below 300°. It was insoluble in organic solvents, but easily soluble in water, from which it was partially precipitated by the addition of strong acids. On the addition of sodium carbonate to its aqueous solution, carbon dioxide was evolved. The substance also gave a test for sulphur when fused with sodium.

Found: C, 56.9; H, 4.8%. E.W. 332. Calculated for C₁₆H₁₃O₄NS.H₂O: C, 57.6; H, 4.5%. E.W. 333.

Attempts to cyclise the amide without concomitant sulphonation were unsuccessful.

2-(α -Naphthamido)-diphenyl, (I, $R=\alpha$ -C₁₀H₇).

The amide, prepared in good yield from *o*-xenylamine (11.3 g.) and α -naphthoyl chloride (13.7 g.) in dry pyridine (20 c.c.) by the usual method, crystallised from alcohol in colourless needles m.p. 142°.

Found: C, 85.2; H, 5.2%. Calculated for C₂₈H₁₇ON: C, 85.4; H, 5.3%.

6-(α -Naphthyl)-phenanthridine, (II, $R=\alpha$ -C₁₀H₇).

Cyclisation of the α -naphthoyl derivative (18 g.) with phosphorus oxychloride (35 c.c.) proceeded easily and in five minutes evolution of hydrogen chloride had nearly ceased. The pure substance (12 g.) formed small colourless plates, m.p. 125°, from methyl alcohol. It was easily soluble in the usual solvents, excepting light petroleum.

Found: C, 90.6; H, 4.8%. Calculated for C₂₈H₁₈N: C, 90.5; H, 4.9%.

The *picrate* crystallised from alcohol in sparingly soluble yellow ferns, melting at 245° with decomposition.

Found: N, 10.3%. Calculated for C₂₈H₁₈O₇N₄: N, 10.5%.

The *methiodide* formed rapidly when the base was heated with excess methyl iodide at 100° in a sealed tube. After thirty minutes, the reaction mixture was diluted with ether and the product collected. It was dimorphous appearing as yellow rods or orange prisms. Both forms separated from alcohol at the same time, irrespective of the seed used, but on standing or more rapidly on rubbing the yellow form disappeared. The orange prisms melted with decomposition at 211°. The pure yellow form was not isolated.

Found: C, 64.6; H, 3.9%. Calculated for C₂₄H₁₈NI: C, 64.4; H, 4.0%.

2-Mesitamido-diphenyl.

Mesitoyl chloride (9 g.) reacted slowly with *o*-xenylamine (16.7 g.) in dry ether (600 c.c.) at room temperature. After standing for two weeks the mixture was refluxed for fifteen hours and then filtered. The filtrate, after washing thoroughly with dilute acid, dilute alkali and water, and drying, was evaporated. Crystallisation of the residue from light petroleum to which a little acetone had been added, yielded the pure substance (4 g.) as colourless needles m.p. 125°.

Found: C, 84.0; H, 6.8%. Calculated for C₂₃H₂₁ON: C, 83.8; H, 6.7%.

6-(2':4':6'-Trimethyl-phenyl)-phenanthridine.

The amide (3.5 g.) was rapidly cyclised by boiling phosphorus oxychloride (7 c.c.), the reaction being substantially complete in five minutes. By working up the reaction mixture in the usual way, a crude product (3 g.) was obtained. Recrystallisation from methyl alcohol afforded large colourless rhombs melting at 157°.

Found: C, 88.3; H, 6.7%. Calculated for C₂₈H₁₈N: C, 88.9; H, 6.4%.

The *picrate* separated from alcohol in microscopic yellow irregular plates melting at 231° with decomposition.

Found: N, 10.8%. Calculated for C₂₈H₂₂O₇N₄: N, 10.6%.

The *methiodide* prepared without difficulty in the usual manner crystallised from acetone ethyl acetate mixture as yellow prisms which began to decompose at 202°.

Found: C, 63.0; H, 4.9%. Calculated for C₂₈H₂₂NI: C, 62.9; H, 5.0%.

It was easily soluble in alcohol and acetone, but only slightly soluble in water and ethyl acetate.

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STUDIES IN THE PHENANTHRIDINE SERIES.

PART IV. 1:10-DIMETHYL PHENANTHRIDINES.

By E. RITCHIE, M.Sc.

Manuscript received, September 21, 1944. Read (in title only), October 4, 1944.

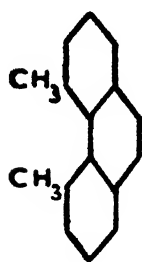
In spite of several attempts to synthesise it, 4:5-dimethyl-phenanthrene (I) has not yet been prepared. These failures are undoubtedly due to the considerable strain which would exist in this molecule, for a scale drawing in which the molecule is planar, shows that the methyl groups interfere with each other to a large extent. However, it has been proved by Newman (1940), who has briefly reviewed this subject, that more complex substances of this type do exist. He succeeded in preparing 4:5-dimethyl-chrysene for example, and in a more recent article Cook (1942) cites additional examples. The successful synthesis of these more complex molecules is probably made possible by their greater flexibility, but it must be pointed out that there is still great resistance to their formation as evidenced by the low yields obtained in their preparation. Substances of this type also have abnormal properties.

The question of the spatial disposition of the methyl groups is an interesting one, and Newman has suggested three alternatives (or a combination thereof): “(1) the methyl groups lie bent away from each other but in the same plane as the aromatic rings; (2) the aromatic rings are distorted in some way; (3) the methyl groups are bent out of the plane of the aromatic rings. Of these, the latter seems more likely. Should this indeed be the case, optical activity would be possible.” A completely satisfactory answer to this question could probably be obtained only by an X-ray crystallographic examination of the substances in question.

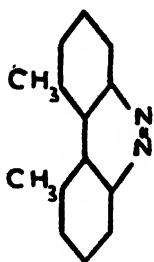
In view of the resistance to the formation of hydrocarbons of the 4:5-dimethyl-phenanthrene type, it was surprising to find in the literature that certain analogously constituted heterocyclic compounds are easily prepared in good yield. Thus 2:2'-dinitro-6:6'-dimethyl-diphenyl readily yields 1:10-dimethyl-benzo(c)cinnoline oxide by sodium sulphide reduction (Sako, 1934), and 1:10-dimethyl-benzo(c)cinnoline (R.I. No. 1909) (II) by sodium amalgam reduction (Keuner and Stubbings, 1921) or by electrolytic reduction (Wittig and Stichnoth, 1935). The latter workers also attempted the optical resolution of this substance but without success, which suggests but does not prove a planar configuration for this molecule. Sako (*loc. cit.*) found that optically active 6-nitro-6'-acetamido-diphenic acid was slowly transformed by hot concentrated sulphuric acid to inactive 10-nitro-phenanthridone-1-carboxylic acid (III). No attempt was made to resolve this substance and since the diphenic acid is readily racemised by mineral acids, no conclusions regarding the configuration of (III) can be drawn from this experiment, as realised by Sako.

These results suggested that a study of the cyclisation of the acyl derivatives of 2-amino-6:6'-dimethyl-diphenyl (V) would contribute useful information to this question. The required base was prepared as follows: By partial reduction (Sako, *loc. cit.*) 2:2'-dimethyl-6:6'-dinitro-diphenyl was converted to 2:2'-dimethyl-6-amino-6'-nitro-diphenyl, which was deaminated by diazotisation and treatment with hypophosphorus acid to 2-nitro-6:6'-dimethyl-diphenyl (IV), a pale yellow solid m.p. 45°. The properties of this substance agreed with

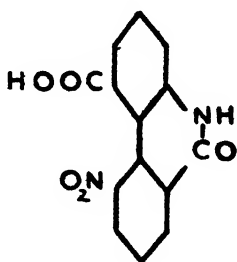
those reported for it by Mascarelli and Angeletti (1938), who obtained it by a slightly different method. Reduction by stannous chloride in acetic-hydrochloric acid yielded the base (V) as a colourless oil boiling at 169-170°/20 m.m. which could not be induced to crystallise, although Mascarelli and Angeletti (*loc. cit.*)



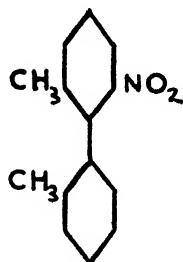
I



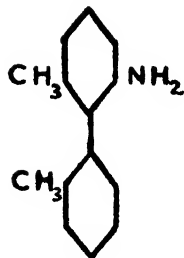
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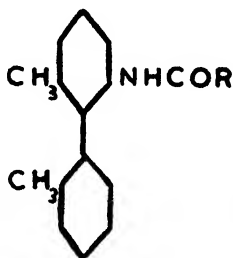
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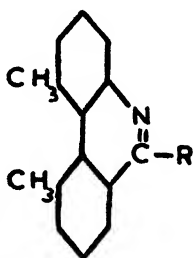
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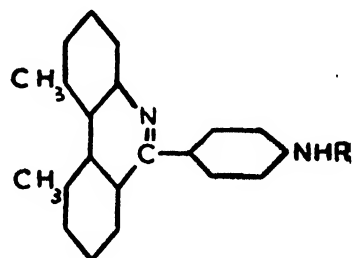
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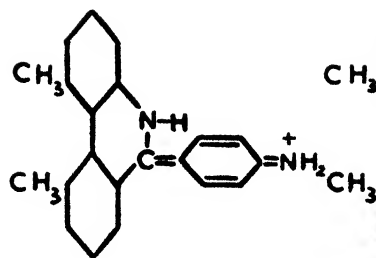
VI



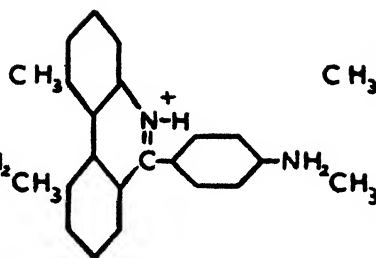
VII



VIII



IX



X

describe it as a pale yellow crystalline powder m.p. 105°. These authors did not characterise their product by the preparation of solid derivatives so further checks were not possible. The base (V) condensed readily with 5-nitro-salicylaldehyde to a yellow crystalline Schiff's base and also yielded a pale yellow p-nitro-benzoyl derivative (VI, $R_2 = p\text{-C}_6\text{H}_4\text{NO}_2$), but the benzoyl derivative (VI, $R_1 = \text{C}_6\text{H}_5$) could not be induced to crystallise.

The cyclisation of these acyl derivatives was carried out with phosphorus oxychloride in nitrobenzene solution at 180° , since it was thought that the 6' methyl group and the p-nitro-phenyl group would retard cyclisation by virtue of their inductive effects. Under these "forcing" conditions cyclisation was rapid and good yields (about 70%) of 1:10-dimethyl-9-phenyl-phenanthridine (VII, $R_1=C_6H_5$) and 1:10-dimethyl-9-(4'-nitro-phenyl)-phenanthridine (VII, $R_2=pC_6H_4NO_2$) were obtained. The former substance was isolated as a gum which could not be crystallised even after regeneration from its picrate and sulphate, both of which were crystalline. However it showed the fluorescence phenomena typical of phenanthridines and its picrate had the correct analytical figures, so there can be no doubt as to its identity. The substance (VII, $R_2=pC_6H_4NO_2$) crystallised from ethyl acetate in pale yellow prisms. When heated, these partially melted at 148° , resolidified and then melted again at 163° . Repeated recrystallisations from a variety of solvents failed to alter this behaviour, and in each case the crystals appeared to be homogeneous. The same double melting point was also observed after the substance had been converted to its picrate (which had a single m.p.) and regenerated. A conclusive proof of its homogeneity was provided by the fact that no bands were formed when it was adsorbed on Brockmann alumina and that the various fractions obtained by elution were identical. There can be no doubt then that 1:10-dimethyl-phenanthridines are capable of existence and that they are readily formed by the application of the Morgan-Walls reaction to appropriately substituted diphenyls.

It was originally intended to reduce the nitro compound to the base (VIII, $R_1=H$) and attempt an optical resolution, but the amine proved to be unsuitable for this purpose. On catalytic reduction the nitro compound took up the theoretical amount of hydrogen (further evidence for its structure and homogeneity) but the amine thus obtained was a glass. From this a crystalline acetyl derivative (VIII, $R_2=COCH_3$) was prepared which was hydrolysed back to the amine, which was then obtained in crystalline form. Purification of this was difficult because of its high solubility in all solvents excepting water and light petroleum, its tendency to separate from mixed solvents as an oil and its discoloration on exposure to the air. The best specimen obtained was light tan. It dissolved in dilute hydrochloric acid to an orange-red solution, changed to yellow by addition of concentrated acid. According to Morgan and Walls (1931, 1938) these colour changes are due to the formation of the resonating ion (IX) by the attachment of a proton to the ring nitrogen in dilute acid and its conversion to the non-resonating ion (X) in concentrated acid by the addition of another proton to the other nitrogen. Now resonance could occur only if the phenanthridine nucleus were planar or nearly so, hence it appears certain that this is the case in the ion (IX). It does not necessarily follow, however, that the phenanthridine nucleus in the free base (VIII, $R_1=H$) and in the other 1:10-dimethyl-phenanthridines is planar or nearly so, since there is probably considerable resonance energy associated with the ion (IX).

EXPERIMENTAL.

Copper Powder.

Wittig and Stichnoth (*loc. cit.*) prepared 2:2'-dimethyl-6:6'-dinitro-diphenyl by heating 2-iodo-3 nitro-toluene with "Naturkupfer C". This grade of copper powder was not available in sufficient quantity, but it was found that copper powder prepared by the following method was equally good.

A solution of copper sulphate (300 g.) in water (1,000 c.c.) was stirred and cooled in running water whilst it was treated gradually with zinc dust (about 90 g.) until decolorised. Addition of the zinc dust was regulated so that the temperature did not rise above 60° . After settling, the supernatant liquid was decanted and the copper washed by decantation successively with

water (twice, 2,000 c.c. each time), dilute hydrochloric acid (twice 2,000 c.c. of N), water (thrice, 2,000 c.c.) and acetone (twice, 1,000 c.c.). It was then transferred to a Buchner funnel with acetone, pressed well and dried for three hours over concentrated sulphuric acid in an evacuated desiccator. The product, which weighed 70-75 g., should be used shortly after its preparation.

2-Nitro-6 : 6'-dimethyl-diphenyl (IV).

The method described by Mascarelli and Angeletti (*loc. cit.*) is much inferior to the one described below.

The ice cold diazo solution prepared from 2 : 2'-dimethyl-6-amino-6'-nitro-diphenyl (69 g.) concentrated hydrochloric acid (207 c.c.), water (420 c.c.) and sodium nitrite (20 g.) in water (40 c.c.) in the usual manner was added in one lot to a solution of potassium hypophosphite (250 g.) in concentrated hydrochloric acid (100 c.c.) and water (625 c.c.) at 0°. The reaction mixture was maintained at this temperature for ten hours and then allowed to come to room temperature during twelve hours. After heating to boiling, the mixture was cooled and extracted with ether. The ethereal extract was washed thoroughly with dilute sodium hydroxide solution and water, dried and distilled. The pure product (40 g.) distilled at 191.2°/20 m.m. as a yellow oil which eventually solidified to a pale yellow solid m.p. 45°.

2-Amino-6 : 6'-dimethyl-diphenyl (V).

To a solution of the nitro compound (36 g.) in glacial acetic acid (400 c.c.) warmed to 70° was added rapidly a solution of stannous chloride (160 g.) in concentrated hydrochloric acid (180 c.c.) warmed to the same temperature. The temperature rose to about 85° and the yellow colour began to fade. After fifteen minutes the reaction mixture was heated on the water bath for one hour, then cooled, diluted and poured into excess dilute sodium hydroxide solution. The product was extracted with ether, dried over solid sodium hydroxide, and then distilled. The pure amine (27 g.) was isolated as colourless oil boiling at 169-170°/20 m.m. which could not be crystallised.

Found : C, 85.1 ; H, 7.4%. Calculated for $C_{14}H_{15}N$: C, 85.3 ; H, 7.6%.

The 5-nitro-salicylidene derivative prepared in the usual manner, crystallised from alcohol in small yellow needles m.p. 108°.

Found : C, 72.4 ; H, 5.4%. Calculated for $C_{21}H_{18}O_3N_2$: C, 72.8 ; H, 5.2%.

2-Benzamido-6 : 6'-dimethyl-diphenyl (VI, $R_1 = C_6H_5$).

A solution of the amine (5 g.) in dry pyridine (10 c.c.) was treated with benzoyl chloride (3.5 g.) and heated on the steam bath for one hour. The product precipitated on pouring the reaction mixture into dilute hydrochloric acid was extracted with ether and the extract washed thoroughly with dilute acid, dilute alkali and water and dried. Evaporation of the ether left a thick colourless syrup (7.5 g.) which could not be crystallised.

2-(p-Nitrobenzamido)-6 : 6'-dimethyl-diphenyl (VI, $R_2 = pC_6H_4NO_2$).

This derivative prepared as above, crystallised from a little alcohol in very pale yellow rectangular plates melting at 122°.

Found : C, 72.5 ; H, 5.4%. Calculated for $C_{21}H_{18}O_3N_2$: C, 72.8 ; H, 5.2%.

1 : 10-Dimethyl-6-(4'-nitro-phenyl)-phenanthridine (VII, $R_2 = pC_6H_4NO_2$).

When a solution of the p-nitrobenzoyl derivative (11.5 g.) in nitrobenzene (30 c.c.) and phosphorus oxychloride (15 c.c.) was heated to 180°, a vigorous reaction set in, and hydrogen chloride was copiously evolved. The vigour of the reaction soon diminished but heating was continued for five hours. After cooling, the reaction mixture was poured into excess dilute ammonia and the nitrobenzene removed by steam distillation. The product which formed a glass on cooling crystallised readily when rubbed in contact with ethyl acetate. Two recrystallisations from alcohol-ethyl acetate yielded the pure product (8 g.) as pale yellow prisms which melted at 148° and then at 163°.

Found : C, 76.5 ; H, 4.9%. Calculated for $C_{21}H_{18}O_2N_2$: C, 76.8 ; H, 4.9%.

The substance was easily soluble in benzene, moderately soluble in ethyl acetate, but only slightly soluble in alcohol. Various tests of the homogeneity of this substance were made as described in the theoretical section above.

The *picrate* separated as bundles of small yellow rods when hot alcoholic picric acid was added to a benzene solution of the base. It melted at 235° with slight darkening.

Found: C, 58.1; H, 3.6%. Calculated for $C_{27}H_{19}O_9N_5$: C, 58.2; H, 3.4%.

1:10-Dimethyl-6-phenyl-phenanthridine (VII, $R_1=C_6H_5$).

Cyclisation of the benzoyl derivative (7.5 g.) carried out as above, yielded a colourless gum (5 g.) which could not be crystallised even after regeneration from its *picrate* or sulphate. In glacial acetic acid or concentrated or dilute sulphuric acid it formed a yellow solution with a green fluorescence.

The *picrate* prepared in alcohol, separated as small yellow elongated plates.

Found: C, 63.2; H, 3.9%. Calculated for $C_{27}H_{20}O_7N_4$: C, 63.3; H, 3.9%.

This substance also has a double melting point. When heated it sinters at 170°, melts at 177°, then solidifies and melts at 199°.

1:10-Dimethyl-6-(4'-acetamido-phenyl)-phenanthridine (VIII, $R_2=COCH_3$).

A solution of the nitro compound (VII, $R_2=p-C_6H_4NO_2$; 12 g.) in the minimum of hot alcohol was shaken in an atmosphere of hydrogen in the presence of Raney nickel. The theoretical amount of hydrogen was taken up without difficulty. After filtering off the catalyst, the filtrate was evaporated leaving a pale yellow glass, which could not be crystallised. However, a crystalline acetyl derivative was readily obtained by the usual methods. The crude substance crystallised once from benzene yielded a nearly pure product (10 g.). The pure substance separates from much aqueous methyl alcohol in small colourless plates, m.p. 199°.

Found: C, 80.5; H, 5.8%. Calculated for $C_{23}H_{20}ON_2$: C, 81.2; H, 5.9%.

It is easily soluble in alcohol and in ethyl acetate but less so in benzene.

1:10-Dimethyl-6-(4'-amino-phenyl)-phenanthridine (VIII, $R_1=H$).

The acetyl derivative (3 g.) was hydrolysed by boiling for three hours with alcoholic potassium hydroxide (100 c.c. of 10%). After removing the alcohol, the mixture was diluted and extracted with benzene. Distillation of the benzene left an orange gum which eventually solidified. Purification of this was difficult but eventually by crystallisation from ether containing a little light petroleum the product was obtained as small light tan needles which melted at 134°.

Found: C, 84.5; H, 6.0%. Calculated for $C_{21}H_{18}N_2$: C, 84.6; H, 6.0%.

It was easily soluble in the usual organic solvents, excepting light petroleum. It dissolved in very dilute hydrochloric acid to an orange-red solution. On the addition of concentrated hydrochloric acid the colour changed to yellow.

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STUDIES IN THE PHENANTHRIDINE SERIES.

PART V. PHENANTHRIDINE-6-ALDEHYDE AND RELATED COMPOUNDS.

By E. RITCHIE, M.Sc.

Manuscript received, September 21, 1944. Read (in title only), October 4, 1944.

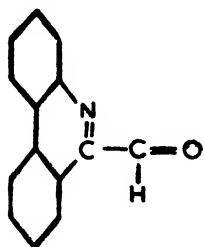
The experiments recorded in Part III of this series show that the application of the Morgan-Walls reaction to acyl derivatives of o-xenylamine cannot always be relied upon to yield the corresponding phenanthridines, particularly when the acyl residue carries reactive atoms or groups. Accordingly another synthesis was sought which would furnish phenanthridines substituted in the 6 position even when the substituents bore reactive groups. The most suitable starting material for such a synthesis appeared to be phenanthridine-6-aldehyde (I), since it has been shown that the similarly constituted quinoline-2-aldehyde and isoquinoline-1-aldehyde possess the normal reactivity of aldehydes (Kwartler and Lindwall, 1937; Burger and Modlin, 1940; Johnson and Hamilton, 1941; Barrows and Lindwall, 1942). It was decided therefore to prepare this substance and examine its behaviour in some common reactions typical of aldehydes.

The α - and γ -aldehydes of the pyridine, quinoline and isoquinoline series have been prepared in poor to moderate yields by oxidising the corresponding methyl derivatives with selenium dioxide (Henze, 1934; Glenn and Bailey, 1941; Kaplan, 1941; Borsche and Hartmann, 1940; and references quoted above). When 6-methyl-phenanthridine was refluxed with selenium dioxide in alcoholic solution the reaction did not proceed smoothly. But when the oxidation was carried out in ethyl acetate, the aldehyde (I) was obtained in about 70% yield. It dissolved easily in dilute hydrochloric acid to a yellow solution which showed a faint blue fluorescence, but all attempts to obtain quaternary ammonium salts from it failed. It was recovered unchanged, except for slight resinification, after heating with excess methyl iodide at 100° for two hours, and was gradually resinified when refluxed with methyl sulphate in toluene. This unreactivity cannot be caused by steric hindrance by the formyl group, since phenanthridines substituted in the 6 position by much bulkier groups react readily under these conditions (Part III), but must be due to the lowered availability of the lone electron pair of the nitrogen for quaternary ammonium salt formation, by conjugation with the strongly electrophilic oxygen of the carbonyl group. This effect is shown diagrammatically in the resonance form (1a).

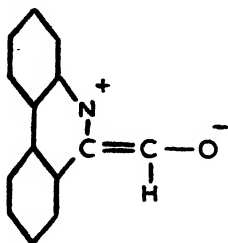
The aldehyde readily yielded an oxime, semicarbazone and phenylhydrazone by the usual methods and also condensed with p-toluidine to a Schiff's base. When oxidised in dilute sulphuric acid solution with the theoretical amount of potassium dichromate, no carboxylic acid was formed; instead the reaction mixture consisted of unchanged aldehyde and phenanthridone. A nearly quantitative yield of the latter substance was obtained when excess of the oxidising agent was used. Under the same conditions phenanthridine and 6-methyl-phenanthridine are unaffected and the facile conversion of the aldehyde to phenanthridone is remarkable. Phenanthridone was also obtained exclusively by oxidation with permanganate in acid solution at 60°, but at 40° in alkaline aqueous acetone, phenanthridine-6-carboxylic acid was the main product. This was easily decarboxylated to phenanthridine as reported by Walls (1934), and hence the sequence, selenium dioxide oxidation, permanganate oxidation,

decarboxylation, provides an alternative method of degrading 6-methylphenanthridines to their parent bases.

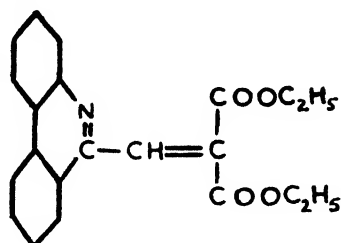
Although quinoline-2-aldehyde is converted to quinaldoin under the conditions of the benzoin condensation (Henze, *loc. cit.*; Kaplan, *loc. cit.*),



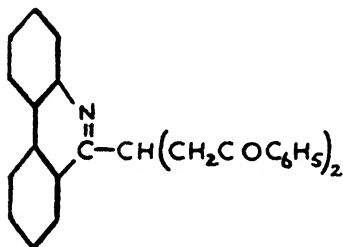
I



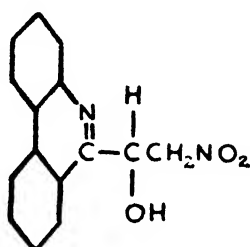
Ia



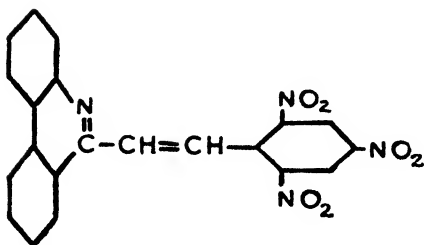
II



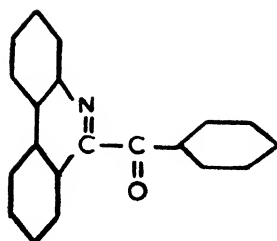
III



IV



V



VI

phenanthridine-6-aldehyde was immediately resinified by potassium cyanide and no crystalline product could be isolated from the reaction mixture. Reduction by formaldehyde in alkaline solution also yielded tars and a similar result attended efforts to apply Döebner's cinchoninic acid synthesis. Some condensations of the aldehyde with reactive methylene groups were then examined. When the aldehyde was heated with malonic acid in pyridine solution in the presence of piperidine, carbon dioxide was evolved but the product was a tar.

However reaction with ethyl malonate proceeded smoothly, yielding crystalline ethyl α -carbethoxy- β -(6-phenanthridyl)-acrylate (II). Only amorphous products were obtained when the aldehyde was condensed with acetone, but from acetophenone there was obtained 6-(diphenacyl-methyl)-phenanthridine (III). Nitromethane also reacted readily with the aldehyde, producing β -hydroxy- β -(6-phenanthridyl)- α -nitroethane (IV), and from trinitrotoluene, ω -(6'-phenanthridyl)-2 : 4 : 6-trinitro-styrene (V) was obtained.

All attempts to oxidise 6-ethyl-phenanthridine by selenium dioxide to 6-acetyl-phenanthridine were unsuccessful, but 6-benzyl-phenanthridine (Part III) was easily converted to 6-benzoyl-phenanthridine (VI) characterised by its oxime, semicarbazone and phenylhydrazone.

Note.—The substances, ethyl α -carbethoxy- β -(6-phenanthridyl)-acrylate (II), γ -(6-phenanthridyl)-butyric acid and δ -(6-phenanthridyl)-valeric acid (Part III) were tested for plant hormone activity by the kindness of Dr. R. N. Robertson of the Botany Department of this University, who reported complete inactivity in each case.

EXPERIMENTAL.

Phenanthridine-6-aldehyde (I).

A solution of 6-methyl-phenanthridine (12 g.) in ethyl acetate (250 c.c.) was treated with finely powdered selenium dioxide (7.6 g.) and the mixture refluxed for ten hours. The selenium which had gradually separated during this time, was filtered from the hot solution and the red filtrate evaporated on the water bath. The dark residue was then extracted with hot dilute hydrochloric acid (250 c.c. of N) and the extract charcoaled, filtered and cooled. By the careful addition of solid sodium carbonate, dark seleniferous compounds were precipitated. These were filtered off and the product recovered by further addition of sodium carbonate. After washing with hot water, it was recrystallised twice from alcohol yielding pale yellow opaque needles (9 g.) which melted at 139°. This melting point was not raised by further recrystallisation.

Found: C, 80.9; H, 4.2%. Calculated for $C_{14}H_9ON$: C, 81.1; H, 4.3%.

It was insoluble in light petroleum, but easily soluble in other organic solvents and in dilute mineral acids.

The *oxime* prepared in the usual manner, crystallised from a large volume of alcohol in small pale yellow plates which melted with decomposition at 227°. It was sparingly soluble in the usual organic solvents.

Found: N, 12.8%. Calculated for $C_{14}H_{10}ON_2$: N, 12.6%.

The *semicarbazone* which is also sparingly soluble in the usual solvents, separated from much alcohol as colourless shining elongated plates, m.p. 238° with decomposition.

Found: N, 21.4%. Calculated for $C_{15}H_{11}ON_4$: N, 21.2%.

The *phenylhydrazone* is moderately soluble in hot alcohol and separated from this solvent in sheaves of golden needles melting at 166°.

Found: N, 14.4%. Calculated for $C_{20}H_{15}N_3$: N, 14.1%.

6-Phenanthridyl-formylidene-p-toluidine, prepared from the aldehyde and p-toluidine in alcohol crystallised in lemon yellow needles, m.p. 87°.

Found: N, 9.5%. Calculated for $C_{21}H_{16}N_2$: N, 9.4%.

Oxidation Experiments.

(1) A solution of the aldehyde (6.2 g.) in water (200 c.c.) and concentrated sulphuric acid (13 c.c.) was stirred and heated on the water bath whilst it was treated with a solution of potassium dichromate (6 g.) in water (100 c.c.) during thirty minutes. Stirring and heating were continued for two hours, then the reaction mixture was diluted and the product (5.8 g.) collected. After purification it was identified as phenanthridone.

(2) A solution of the aldehyde (2.1 g.) in water (50 c.c.) and concentrated sulphuric acid (3 c.c.) was stirred and maintained at 60° whilst 1% potassium permanganate solution was slowly added. The reaction appeared to be completed when about 125 c.c. had been added. After the

addition of a little sulphurous acid to dissolve some manganese dioxide which had separated, the product (1.9 g.) was collected. It was identified as phenanthridone.

(3) A solution of potassium permanganate (1.5 g.) in water (30 c.c.) was added during thirty minutes to a solution of the aldehyde (3 g.) in acetone (150 c.c.) stirred and kept at 40-45°. After stirring and warming for another thirty minutes sufficient sulphurous acid was added to dissolve the precipitated manganese dioxide, followed by dilute hydrochloric acid (40 c.c. of N). Then the acetone was boiled off and the product collected. Extraction of this with hot dilute sodium hydroxide solution (100 c.c. + 50 c.c. of 5%) left a residue of phenanthridone (0.8 g.). Acidification of the alkaline extract afforded phenanthridine-6-carboxylic acid (1.8 g.), which evolved carbon dioxide at 155°, leaving phenanthridine.

Ethyl α -carbethoxy- β -(6-phenanthridyl)-acrylate (II).

A solution of the aldehyde (2 g.) and diethyl malonate (1.5 g.) in absolute alcohol (40 c.c.) was treated with a few drops of piperidine and allowed to stand at room temperature. After standing for about three weeks, the solvent was evaporated and the residual oil rubbed with a little acetone. The product which slowly solidified was drained on a porous tile. The pure substance (0.8 g.) obtained by two crystallisations from methanol, formed very pale yellow flat needles m.p. 91°. It was easily soluble in the usual organic solvents excepting light petroleum.

Found : C, 72.4; H, 5.6%. Calculated for $C_{21}H_{19}O_4N$: C, 72.2; H, 5.4%.

6-(Diphenacyl-methyl)-phenanthridine (III).

When a solution of the aldehyde (2 g.) and acetophenone (1.8 g.) in alcohol (40 c.c.) was treated at room temperature with aqueous sodium hydroxide (20 c.c. of 10%) it immediately darkened in colour and in a short time the product began to separate. After half an hour it was collected, and washed with alcohol and water. Recrystallised from alcohol it (2 g.) formed dull yellow needles with a faint green tinge, which melted at 157°.

Found : C, 84.1; H, 5.3%. Calculated for $C_{30}H_{23}O_2N$: C, 83.9; H, 5.3%.

β -Hydroxy- β -(6-phenanthridyl)- α -nitroethane (IV).

A solution of the aldehyde (2 g.) and nitromethane (2 c.c. excess) in alcohol (50 c.c.) was treated at room temperature with piperidine (0.5 c.c.). After standing for a few hours the product began to crystallise in rosettes of slender needles, which were collected after two days and washed with a little alcohol. The pure product (1.2 g.) crystallised from this solvent in nearly colourless needles which began to decompose at 132°.

Found : N, 10.7%. Calculated for $C_{15}H_{12}O_3N_2$: N, 10.5%.

ω -(6'-Phenanthridyl)-2 : 4 : 6-trinitro-styrene (V).

Trinitrotoluene (1.1 g.) and the aldehyde (1 g.) were dissolved in hot alcohol (30 c.c.) and a few drops of piperidine added. The solution immediately became red and in a short time the product began to crystallise out. After cooling the nearly theoretical yield was collected and washed with alcohol. The substance crystallised from benzene in almost colourless fibrous needles which began to decompose at 180°.

Found : N, 13.4%. Calculated for $C_{41}H_{12}O_6N_4$: N, 13.5%.

It was only slightly soluble in the usual organic solvents.

6-Benzoyl-phenanthridine (VI).

When a solution of 6-benzyl-phenanthridine (5.2 g.) and selenium dioxide (2.3 g.) in alcohol (200 c.c.) was refluxed, selenium began to separate almost immediately. After ten hours, the hot solution was filtered and the filtrate evaporated on the water bath. The residue was extracted with ethyl acetate, the extract charcoaled filtered and evaporated. The product which was now almost free of selenium compounds, was recrystallised three times from alcohol with the aid of charcoal, yielding finally the pure substance (3.5 g.) as colourless hair-like crystals which melted

at 152°. It was easily soluble in benzene, acetone and ethyl acetate, moderately in hot alcohol, but sparingly in cold alcohol.

Found: C, 84.2; H, 4.9%. Calculated for $C_{20}H_{13}ON$: C, 84.8; H, 4.6%.

The *oxime* crystallised from ethyl alcohol in colourless prismatic needles which began to darken at 210° and then decomposed at 217°.

Found: N, 9.0%. Calculated for $C_{20}H_{14}ON_2$: N, 9.1%.

The *semicarbazone* separated from ethyl alcohol in colourless plates melting at 175°.

Found: N, 16.8. Calculated for $C_{21}H_{16}ON_4$: N, 16.5%.

The *phenylhydrazone* crystallised from alcohol benzene in small yellow leaflets which melt at 92°.

Found: N, 11.6%. Calculated for $C_{26}H_{19}N_3$: N, 11.3%.

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STUDIES IN THE PHENANTHRIDINE SERIES.

PART VI. A SYNTHESIS OF 3-METHYL PHENANTHRIDINE.

By E. RITCHIE, M.Sc.

Manuscript received, September 21, 1944. Read (in title only), October 4, 1944.

Of the nine possible mono-methyl phenanthridines, only three are described in the literature, and all of these were first synthesised by Pictet and his collaborators. The 6 isomer was obtained by fusing 2-acetamido-diphenyl with zinc chloride (Pictet and Hubert, 1896), a reaction later improved by using phosphorus oxychloride to effect the cyclisation (Morgan and Walls, 1931). The 2 and 4 isomers were prepared by pyrolysing benzylidene p- and o-toluidines respectively (Pictet and Ehrlich, 1891) but the method was troublesome and gave poor yields. These two substances were later synthesised by a different method by Kenner, Ritchie and Statham (1937), who condensed p- and o-toluidines, respectively with 2-hydroxymethyl-cyclohexanone and dehydrogenated the resulting tetrahydro-phenanthridines. The synthesis of 3-methyl-phenanthridine has now been achieved by a method which could also be readily adapted to the synthesis of 1-, 2-, or 4-methyl-phenanthridine.

Although Grieve and Hey (1932) failed to obtain 2-nitro-4-methyl-diphenyl (I) by the action of diazotised 3-nitro-4-amino-toluene on benzene in the presence of alkali, this reaction was found to proceed smoothly and afforded (I) in 40% yield, when the general conditions for the Gomberg reaction, recommended by Elks, Haworth and Hey (1940), were adopted. The nitro compound was catalytically reduced in good yield to the amine (II), from which an acetyl derivative (III, $R_1=CH_3$), melting at 148° , and a benzoyl derivative (III, $R_2=C_6H_5$), melting at 92° , were prepared by the usual methods. By oxidation with permanganate in neutral solution (III, $R_1=CH_3$) was converted to 2-acetamido-diphenyl-4-carboxylic acid (IV) melting at 225° . These three substances (III, $R_1=CH_3$, $R_2=C_6H_5$ and IV) have been prepared by Grieve and Hey (*loc. cit.*), who obtained them from a by-product of the nitration of 4-methyl-diphenyl, and who reported for them, melting points of 145° , 221° and 222° respectively. The wide divergence in the values of the melting point of the benzoyl derivative is possibly due to these authors confusing it with the melting point of the acid (IV) during transcription.

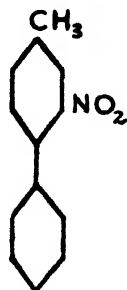
By boiling with phosphorus oxychloride the acetyl derivative was cyclised to 3:6-dimethyl-phenanthridine (V, $R_1=CH_3$) and the benzoyl derivative likewise yielded 3-methyl-6-phenyl-phenanthridine (V, $R_2=C_6H_5$), a further proof of its constitution. On oxidation with potassium dichromate in glacial acetic acid solution, the dimethyl-phenanthridine formed 3-methyl-phenanthridone (VI), the 3-methyl group being unattacked under these conditions. When distilled with zinc dust, the latter substance afforded 3-methyl-phenanthridine (VII), which was readily characterised by its picrate.

EXPERIMENTAL.

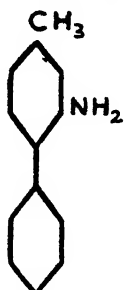
2-Nitro-4-methyl-diphenyl (I).

The diazo solution prepared from 3-nitro-4-amino-toluene (71 g.) concentrated hydrochloric acid (180 c.c.), water (100 c.c.), sodium nitrite (35 g.) and water (70 c.c.) was added to benzene
OO—October 4, 1944.

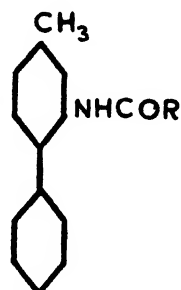
(1,000 c.c.), vigorously stirred and cooled in an ice bath. Then a solution of sodium acetate (180 g.) in water (350 c.c.) was added at such a rate that the temperature of the mixture did not exceed 10° . The reaction was allowed to proceed at 5° - 10° for three hours, then the cooling bath was removed and vigorous stirring continued at room temperature for forty-eight hours.



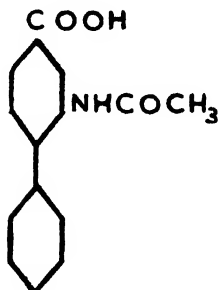
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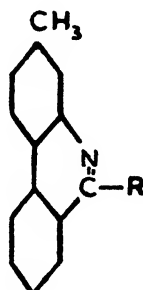
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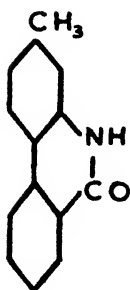
III



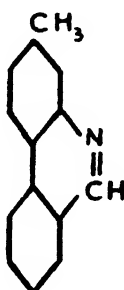
IV



V



VI



VII

The organic layer was separated, the benzene distilled off and the residue distilled under reduced pressure. The fraction boiling at 200 - $230^{\circ}/30$ m.m. was taken up in ether, and the ethereal solution washed thoroughly with hydrochloric acid, sodium hydroxide solution and water. The residue left after removing the ether was fractionated twice under reduced pressure, giving finally a pale orange oil (40% yield), which boiled at $207.9^{\circ}/28$ m.m.

Found : C, 73.6 ; H, 5.0%. Calculated for $C_{13}H_{11}O_2N$: C, 73.2 ; H, 5.1%.

2-Amino-4-methyl-diphenyl (II).

When a warm solution of the nitro compound (I; 10 g.) in alcohol (100 c.c.) was shaken in an atmosphere of hydrogen at normal pressure in the presence of Raney nickel catalyst, slightly more than the theoretical amount of hydrogen was rapidly absorbed. After filtering off the catalyst, the filtrate was distilled, finally under reduced pressure, giving the amine in nearly quantitative yield as a clear colourless oil, boiling at $193.4^{\circ}/29$ m.m.

Found: C, 84.7; H, 7.3%. Calculated for $C_{13}H_{13}N$: C, 85.2; H, 7.1%.

The *picrate* crystallised from alcohol in old gold needles which melted and decomposed at 161° .

Found: N, 13.4%. Calculated for $C_{13}H_{13}O_7N_4$: N, 13.6%.

The *p-nitrosalicylidene* derivative separated from much alcohol in fine yellow needles, m.p. 216° .

Found: N, 8.3%. Calculated for $C_{20}H_{16}O_3N_2$: N, 8.4%.

2-Acetamido-4-methyl-diphenyl (III, $R_1=CH_3$).

Acetylation of the base with acetic anhydride in the usual manner yielded the acetyl derivative which crystallised from aqueous alcohol in colourless glistening flattened needles, m.p. 148° .

Found: N, 6.2%. Calculated for $C_{15}H_{15}ON$: N, 6.2%.

2-Benzamido-4-methyl-diphenyl (III, $R_2=C_6H_5$).

A solution of the amine (II; 9 g.) in dry pyridine (25 c.c.) was treated with benzoyl chloride (7 g.) and heated on the water bath for one hour. The oil which separated on pouring the reaction mixture into dilute hydrochloric acid soon solidified. The product, recrystallised from a little alcohol, formed colourless needles which melted at 92° .

Found: C, 83.9; H, 6.0%. Calculated for $C_{20}H_{17}ON$: C, 83.6; H, 6.0%.

2-Acetamido-diphenyl-4-carboxylic Acid (IV).

This substance was prepared according to the directions of Grieve and Hey (*loc. cit.*). The pure material crystallised from aqueous alcohol in colourless needles, m.p. 225° (lit. 222°).

Found: C, 71.1; H, 5.3%. Calculated for $C_{18}H_{13}O_3N$: C, 70.6; H, 5.1%.

3:6-Dimethyl-phenanthridine (V, $R_1=CH_3$).

When the acetyl derivative (III, $R_1=CH_3$; 9 g.) was refluxed with freshly distilled phosphorus oxychloride (15 c.c.) in a dry atmosphere, clouds of hydrogen chloride were evolved and after about five minutes a yellow solid separated from the reaction mixture. After heating for one hour, the excess phosphorus oxychloride was distilled off under reduced pressure. The residue was extracted with hot hydrochloric acid (250 c.c. of N), the extract filtered and basified with ammonia. The precipitated oil was taken up in ether and the ethereal solution washed and dried. The solid (6.5 g.) remaining after removal of the ether, crystallised from light petroleum ($60-80^{\circ}$) in large prisms which melted at 101° .

Found: C, 87.3; H, 6.4%. Calculated for $C_{18}H_{13}N$: C, 87.0; H, 6.2%.

The *picrate* separated as small yellow needles when hot alcoholic solutions of its components were mixed. It melted with decomposition at 240° .

Found: N, 13.0%. Calculated for $C_{21}H_{16}O_7N_4$: N, 12.9%.

The *methosulphate* was prepared by treating a solution of the base (2 g.) in dry nitrobenzene (15 c.c.) at 180° with methyl sulphate (1.3 g.). The product which had begun to separate immediately, was collected on cooling, washed with ether and recrystallised from alcohol. It formed pale yellow needles which melted and decomposed at 227° . Solutions in water or alcohol had an intense blue fluorescence.

Found: C, 61.6; H, 5.9%. Calculated for $C_{17}H_{13}O_4NS$: C, 61.3; H, 5.7%.

The *methiodide* obtained by heating the base with excess methyl iodide in a sealed tube at 100° for thirty minutes, crystallised from water in fine yellow needles m.p. 278° with decomposition. Solutions of this substance in alcohol or water also had a strong blue fluorescence.

Found: C, 54.8; H, 4.7%. Calculated for $C_{14}H_{14}NI$: C, 55.0; H, 4.6%.

3-Methyl-6-phenyl-phenanthridine (V, $R_2=C_6H_5$).

Cyclisation of the benzamido-methyl-diphenyl (III, $R_2=C_6H_5$; 19 g.) with phosphorus oxychloride (25 c.c.) proceeded smoothly. The residue remaining after removal of the excess phosphorus oxychloride was warmed with ammonia and the liberated base (17.5 g.) isolated with the aid of ether. The substance crystallised from methyl alcohol in colourless needles m.p. 120°.

Found: C, 89.3; H, 5.8%. Calculated for $C_{20}H_{14}N$: C, 89.2; H, 5.6%.

The *picrate* prepared in alcohol formed slender lemon yellow needles decomposing at 243°.

Found: N, 11.4%. Calculated for $C_{24}H_{18}O_7N_4$: N, 11.2%.

The *methosulphate* prepared in nitrobenzene as above, crystallised from alcohol in rosettes of long pale greenish yellow needles, melting at 259°.

Found: C, 67.0; H, 5.3%. Calculated for $C_{22}H_{21}O_4NS$: C, 66.8; H, 5.3%.

Solutions in alcohol had an intense blue fluorescence.

3-Methyl-phenanthridone (VI).

A solution of 3:6-dimethyl-phenanthridine (10 g.) in glacial acetic acid (75 c.c.) was heated on the water bath and stirred whilst it was treated during thirty minutes with powdered potassium dichromate (23 g.). After refluxing for ninety minutes, the reaction mixture was poured into warm dilute hydrochloric acid. The product was collected, washed well with water and then with a little warm alcohol. After drying, the light brown material (6.2 g.) was recrystallised from nitrobenzene, affording long colourless needles which melted at 251°. It was sparingly soluble in the usual organic solvents.

Found: C, 80.0; H, 5.5%. Calculated for $C_{14}H_{11}ON$: C, 80.4; H, 5.4%.

3-Methyl-phenanthridine (VII).

An intimate mixture of 3-methyl-phenanthridone (3 g.) and zinc dust (50 g.) was loosely packed into a hard glass tube sealed at one end, and then heated in a furnace. The greenish yellow fluorescent distillate was dissolved in ether, the solution washed with water, and dried. The oil (1.2 g.) remaining after removal of the ether solidified on rubbing. After several crystallisations from light petroleum (60-80°) the product was obtained as rosettes of colourless needles melting at 81°.

Found: C, 86.7; H, 5.7%. Calculated for $C_{14}H_{11}N$: C, 87.0; H, 5.7%.

It was easily soluble in the usual organic solvents. Solutions in dilute acids showed a marked blue fluorescence.

The *picrate* separated as minute yellow needles m.p. 251° with decomposition, when hot alcoholic solutions of its components were mixed.

Found: N, 13.6%. Calculated for $C_{20}H_{14}O_7N_4$: N, 13.3%.

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STUDIES IN THE PHENANTHRIDINE SERIES.

PART VII. A SYNTHESIS OF BENZO(C)PHENANTHRIDINE.

By E. RITCHIE, M.Sc.

Manuscript received, September 21, 1944. Read (in title only), October 4, 1944.

By distilling the alkaloids, chelerythrine chloride, sanguinarine and chelidonine with zinc dust, Späth and Kuffner (1931 (a), 1931 (b)) isolated a substance $C_{17}H_{11}N$ which they identified with the α -naphthaphenanthridine (benzo(c)phenanthridine, R.I. No. 2740) of Graebe (1904), who had obtained it by a series of reactions from chrysene quinone. The constitution of his product was not strictly proven by Graebe, there being a remote possibility that it was β -naphthaphenanthridine (benzo(i)phenanthridine, R.I. No. 2741). However the structures assigned to these two substances by Graebe were confirmed later by the work of Kenner, Ritchie and Statham (1937), who synthesised the α -naphthaphenanthridine by condensing α -naphthylamine with 2-hydroxy-methyl-cyclohexanone and dehydrogenating the resulting benzotetra-hydro-phenanthridine. A further synthesis of benzo(c)phenanthridine is described below.

2-Phenyl-naphthalene, which is now readily accessible (Elks, Haworth and Hey, 1940) was nitrated to 1-nitro-2-phenyl-naphthalene (Hey and Lawton, 1940) which was catalytically reduced to the amine (I). The acetyl derivative (II) of this (Hey *et al.*, *loc. cit.*) was readily cyclised by boiling phosphorus oxychloride to 6-methyl-benzo(c)phenanthridine (III), which was converted to benzo(c)-phenanthridine by two routes. Firstly, oxidation by potassium dichromate in acetic acid gave benzo(c)phenanthridone (IV), which on distillation with zinc dust yielded the desired product (VII), as reported by Graebe (*loc. cit.*). Secondly, condensation with formaldehyde to 6-($\beta\beta'$ -dihydroxy-isopropyl)-benzo(c)phenanthridine (V), followed by oxidation with Kiliani's dichromate mixture, gave the carboxylic acid (VI). This acid rapidly split out carbon dioxide when heated slightly above its melting point, leaving (VII).

The behaviour of this substance with methylating agents is noteworthy. When heated with excess methyl iodide at 100° in a sealed tube reaction was not complete even after eight hours. Methylation by methyl sulphate in boiling toluene proceeded more rapidly and appeared to be complete in about five hours. This unreactivity must be attributed to steric hindrance by carbon atom 4 and its attached hydrogen atom. When heated, the yellow methiodide gradually became red and at 195° it decomposed, evolving methyl iodide and leaving benzo(c)phenanthridine, identified by a mixed melting point after purification.

EXPERIMENTAL.

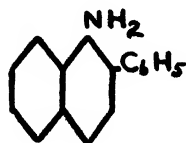
1-Amino-2-phenyl-naphthalene (I).

Catalytic reduction of 1-nitro-2-phenyl-naphthalene (10 g.) in hot alcohol (250 c.c.) in the presence of Raney nickel proceeded slowly at atmospheric pressure, but eventually the theoretical amount of hydrogen was taken up. The product purified from methyl alcohol melted at 105° (lit. 104°) and formed colourless needles.

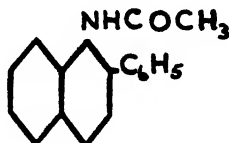
The acetyl derivative (II), prepared in the usual way, was found to melt at 234° in agreement with Hey and Lawton (*loc. cit.*).

6-Methyl-benzo(c)phenanthridine (III).

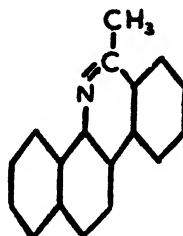
When the acetyl derivative (5 g.) was heated with phosphorus oxychloride (15 c.c.) it rapidly dissolved and hydrogen chloride was evolved. After five minutes' refluxing a solid began to separate from the reaction mixture, but heating was continued for one hour. Then the excess



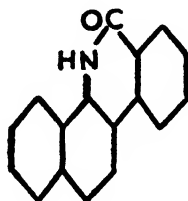
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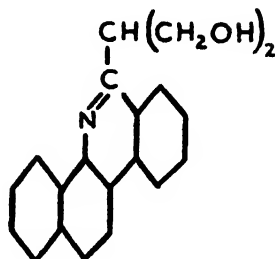
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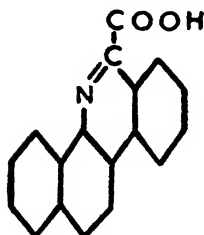
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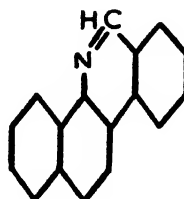
IV



V



VI



VII

phosphorus oxychloride was removed under reduced pressure and the residue shaken with ammonia and ether until no solid remained. After drying, the ether was distilled off, leaving a pale yellow solid (4.2 g.). The product obtained after recrystallisation from light petroleum (60-80°) formed colourless prisms melting at 117°.

Found : C, 88.2 ; H, 5.6%. Calculated for $C_{18}H_{15}N$: C, 88.9 ; H, 5.3%.

The *picrate* crystallised from much alcohol in small bright yellow needles, melting at 233° with decomposition.

Found: N, 12.1%. Calculated for $C_{24}H_{18}O_7N_4$: N, 11.9%.

Benzo(c)phenanthridone (IV).

A stirred solution of methyl-benzophenanthridine (1.8 g.) in glacial acetic acid (50 c.c.) was heated on the water bath and treated during thirty minutes with powdered potassium dichromate (3.4 g.). Then after refluxing for two hours, the reaction mixture was diluted with water, and the product collected. It was washed successively with water, hot dilute sulphuric acid, boiling alcohol and hot glacial acetic acid. The crude product (1.1 g.) after two crystallisations from nitrobenzene afforded light brown needles m.p. 314° (corrected 329°) not changed by further recrystallisation. Graebe (*loc. cit.*) reported m.p. 332.5°.

Found: C, 83.5; H, 4.3%. Calculated for $C_{17}H_{11}ON$: C, 83.2; H, 4.6%.

Distillation of this substance with zinc dust in the manner described by Graebe (*loc. cit.*) eventually yielded *benzo(c)phenanthridine* m.p. 135°, identical with the substance obtained below.

6-(ββ'-dihydroxy-isopropyl)-benzo(c)phenanthridine (V).

A solution of (III; 7 g.) in alcohol (150 c.c.) and aqueous formaldehyde (50 c.c. of 40%) was refluxed for eight hours and then evaporated to a small bulk. The residue was then dissolved in a mixture of alcohol (50 c.c.) and aqueous formaldehyde (50 c.c. of 40%) and refluxing continued for thirty hours. The thick syrup obtained on evaporation of the reaction mixture was boiled down several times with benzene to free it of formaldehyde and yielded finally a colourless crystalline solid. Recrystallisation of this from alcohol-benzene (1:10) afforded the pure substance (6.4 g.) as colourless needles which melted at 169°.

Found: C, 79.0; H, 5.7%. Calculated for $C_{20}H_{17}O_2N$: C, 79.2; H, 5.6%.

The substance was very slightly soluble in light petroleum, but fairly easily soluble in other organic solvents. Its solutions in hot dilute mineral acids were yellow with a blue fluorescence.

Benzo(c)phenanthridine-6-carboxylic Acid (VI).

The glycol (V; 10.1 g.) was refluxed gently with dilute sulphuric acid (100 c.c. of 2N) and the suspension so obtained treated during thirty minutes with Kiliani's dichromate mixture (135 g.). After refluxing for another three hours the reaction mixture was diluted, the product collected and washed well with water. The crude acid was purified by dissolving in hot dilute ammonia, charcoaling, and reprecipitating with acetic acid. It (6.5 g.) then formed a pale yellow powder, m.p. 198°, with evolution of carbon dioxide, which could not be satisfactorily recrystallised.

Benzo(c)phenanthridine (VII).

The crude acid (6 g.) was heated to 210° in an oil bath. In five minutes evolution of carbon dioxide had almost ceased, but heating was continued for another five minutes. After cooling, the crystalline solid was dissolved in ether and the ethereal solution charcoaled, washed with dilute sodium hydroxide solution and water, dried and evaporated. The pale yellow residue (4.5 g.) was recrystallised from alcohol with the aid of charcoal, yielding small colourless plates melting at 135° (lit. 135°).

Found: C, 88.7; H, 4.6%. Calculated for $C_{17}H_{11}N$: C, 89.0; H, 4.8%.

The *picrate* prepared in alcohol formed very sparingly soluble yellow microscopic crystals which melted and decomposed at 255.6° (lit. 256°).

Found: N, 12.4%. Calculated for $C_{23}H_{14}O_7N_4$: N, 12.2%.

5-Methyl-benzo(c)phenanthridinium iodide.

When the base (VII) was heated with excess methyl iodide in a sealed tube at 100°, reaction took place very slowly and was not complete even after eight hours. The product was collected,

washed well with dry ether and recrystallised from water, separating as small bright yellow plates. When heated it gradually became red until at 195° it decomposed, evolving a gas. The residue was identified as benzo(c)phenanthridine.

Found : C, 58.0 ; H, 3.9%. Calculated for $C_{15}H_{14}NI$: C, 58.2 ; H, 3.8%.

5-Methyl-benzo(c)phenanthridinium metho-sulphate.

A solution of the base (2 g.) in dry toluene (25 c.c.) and methyl sulphate (1.1 g.) was refluxed for five hours. The product, which had gradually separated during this period, was collected, washed with ether and recrystallised from alcohol, forming small colourless needles which melted at 217° with decomposition.

Found : C, 64.4 ; H, 4.9%. Calculated for $C_{15}H_{11}O_4NS$: C, 64.2 ; H, 4.8%.

The substance was easily soluble in cold water and in hot alcohol, in which solvents it had a greenish blue fluorescence. Treatment of the aqueous solution with potassium iodide solution precipitated the methiodide.

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Späth, E., and Kuffner, P., 1931a. *Ber. dtsch. chem. Ges.*, 64, 370.
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STUDIES IN THE PHENANTHRIDINE SERIES.

PART VIII. 3 : 8-DIAMINO-PHENANTHRIDINE AND RELATED SUBSTANCES.

By E. 'RITCHIE, M.Sc.

Manuscript received, September 21, 1944. Read (in title only), October 4, 1944.

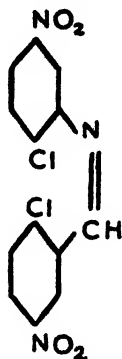
A number of phenanthridine derivatives prepared by Morgan and Walls (1938) were tested for antiseptic activity by Browning, Gulbransen and Robb (1938), who found that two of them, 2-amino-6-(4'-amino-phenyl)-phenanthridine methochloride and 8-amino-6-(4'-amino-phenyl)-phenanthridine methochloride showed some promise. It was also found that the latter substance and the diacetyl derivative of the former had some trypanocidal value (Browning, Morgan, Robb and Walls, 1938). However no derivatives in which both amino groups were directly attached to the phenanthridine nucleus were prepared and tested. In view of the antiseptic activity of the well-known "proflavine" (3 : 6-diamino-acridine) it was decided to attempt the preparation of its formal phenanthridine analogue, 3 : 8-diamino-phenanthridine. Although this object was not accomplished, it is felt that the results obtained possess sufficient interest to warrant recording them.

Kondo and Uyeo (1935, 1937) have synthesised a number of derivatives of phenanthridine by condensing substituted o-bromobenzaldehydes with substituted o-bromoanilines and heating the resulting Schiff's bases with copper powder at 200°. The yields obtained in the latter reaction are very low, being usually about 1%, but it was thought that much better results would be obtained if both halogen atoms were activated by nitro-groups para to them. Accordingly 2 : 2'-dichloro-5 : 5'-dinitro-benzylidene-aniline (I), prepared from 2-chloro-5-nitro-aniline and 2-chloro-5-nitro-benzaldehyde, was heated with copper powder. But in spite of numerous attempts made under a large variety of conditions and with several grades of copper powder, none of the desired product could be isolated. The starting material was either recovered unchanged or converted to amorphous materials.

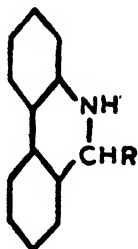
However, an explanation can be given for this result and for the poor yields obtained by Kondo and Uyeo. It has been shown by dipole moment measurements (De Gaouck and Le Fevre, 1938, 1939) that Schiff's bases have a trans, not a cis configuration, and hence the two aromatic nuclei of such molecules cannot easily approach one another sufficiently closely at the temperature of the reaction to allow the formation of a bond between them, even after the removal of the halogen atoms by the copper.

In the second attempt to synthesise 3 : 8-diamino-phenanthridine, dihydro-phenanthridine (II, R=H) served as the starting material. By reducing phenanthridine with tin and hydrochloric acid Pictet and Ankersmit (1891) obtained this substance, which they described as crystallising from dilute alcohol in fine colourless needles melting at 90° and giving blue fluorescent solutions in neutral solvents. On repeating the preparation it was found that dihydro-phenanthridine crystallised from aqueous alcohol in lustrous irregular plates melting at 123°. The solid itself as well as its solutions in neutral solvents showed a striking blue fluorescence, which disappeared on the addition of acid.

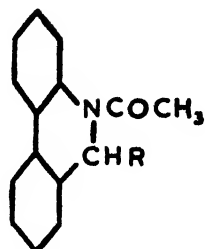
There can be no doubt that the material described by the above authors was very impure. This is understandable since the substance is unstable and a specimen exposed to the air or even kept in a tightly stoppered tube soon becomes



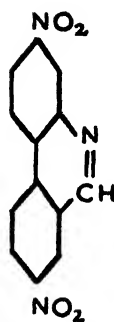
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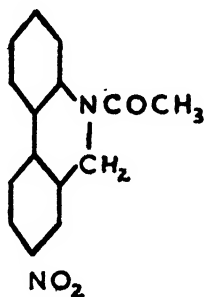
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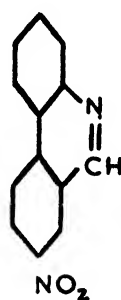
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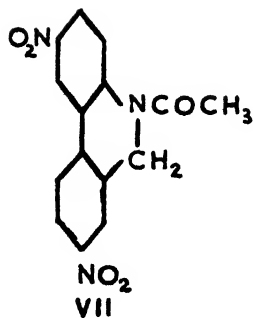
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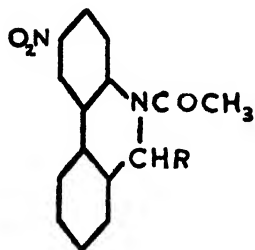
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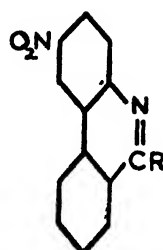
VI



VII



VIII



IX

yellow and its melting point falls. However the acetyl derivative (III, R=H) was quite stable and in agreement with Pictet and Ankersmit it was found to melt at 108°.

Dihydrophenanthridine may be regarded as a secondary amine of the diphenyl series. It was therefore anticipated that it would be dinitrated in excess concentrated sulphuric acid to 3:8-dinitro-dihydrophenanthridine,

which it was then intended to oxidise to 3 : 8-dinitro-phenanthridine, since it had been found that dihydrophenanthridine was easily and quantitatively oxidised to phenanthridine by potassium permanganate. But in all the nitration experiments which were carried out under a variety of conditions the dihydrophenanthridine was converted to dark amorphous products. Occasionally it was possible to isolate a crystalline substance from this, but the yield was so small that further experiments with it were not justified. According to its analytical figures, this substance is a dinitro-phenanthridine, possibly the required one (IV), but in view of the unsatisfactory nature of the reaction by which it was formed it may well be an isomer of this.

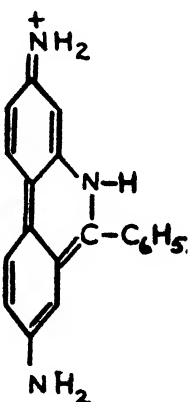
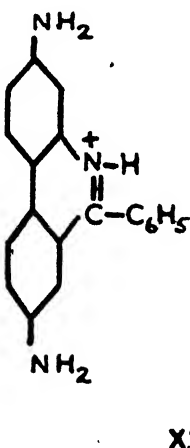
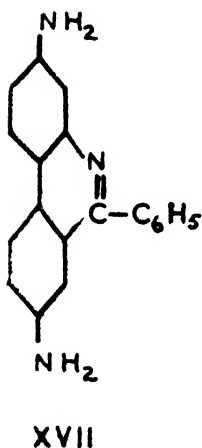
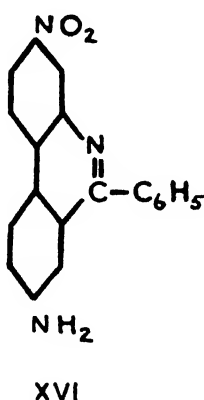
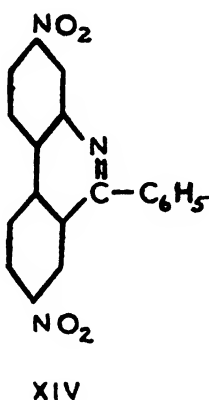
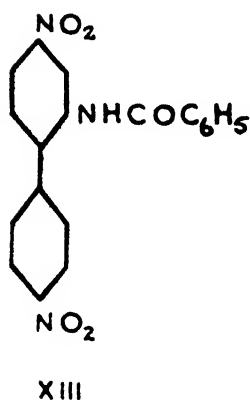
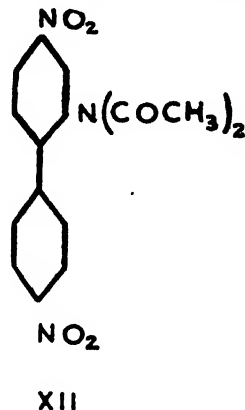
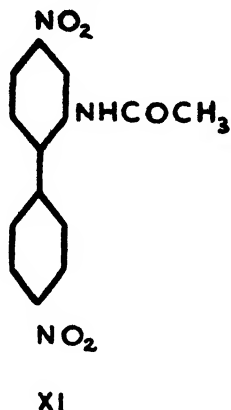
While the substance was at hand some nitration experiments were also carried out on 5-acetyl-dihydrophenanthridine (III, R=H). When nitrated in sulphuric and acetic acid solution under the conditions which convert 2-acetamido-diphenyl to its 4'-nitro derivative (Scarborough and Waters, 1927), it yielded a mixture which appeared to consist of a large amount of one substance and much smaller amounts of two others. Purification was tedious and involved considerable loss of material, but there was finally isolated a pure product, which is almost certainly 8-nitro-5-acetyl-dihydrophenanthridine (V). On hydrolysis with alcoholic hydrochloric acid it was converted in poor yield to a substance which was evidently the related nitro-phenanthridine (VI), since (a) it was stable to oxidation by permanganate in boiling acetone or by dichromate in boiling dilute sulphuric acid, and (b) it could not be acetylated even under the most vigorous conditions. The poor yield obtained suggested that the nitro-group and not atmospheric oxygen was responsible for the oxidation accompanying hydrolysis. This was confirmed by the observation that hydrolysis of 5-acetyl-dihydrophenanthridine under the same conditions yielded dihydrophenanthridine. When a larger proportion of nitric acid was used in the nitration, the product was a thick dark oil. However a dinitro compound, possibly 2 : 8-dinitro-5-acetyl-dihydrophenanthridine (VII), was isolated from this but the yield was so small that it was not further investigated.

Much better results were obtained when the nitration was carried out in acetic acid solution, and the product was then readily isolated in good yield. Under similar conditions Bell (1928) found that 2-acetamido-diphenyl was nitrated in the 5 position and hence the substance obtained in the present experiments was formulated as 2-nitro-5-acetyl-dihydro-phenanthridine (VIII, R=H), a supposition later proved to be correct. On boiling with alcoholic hydrochloric acid, it hydrolysed and oxidised to 2-nitro-phenanthridine (IX, R=H). This substance which melts at 263° is possibly identical with the nitro-phenanthridine m.p. 260-2° of unknown constitution obtained by Morgan and Walls (1932) as one of the products of the direct nitration of phenanthridine.

The constitution of the nitro compound (IX, R=H) was established by submitting 6-methyl-phenanthridine to the same series of reactions as those used in the preparation of (IX, R=H) from phenanthridine. Reduction by tin and hydrochloric acid yielded 6-methyl-dihydrophenanthridine (II, R=CH₃) which had properties similar to those of its lower homologue but was rather more stable. Nitration of the acetyl derivative (III, R=CH₃) gave (VIII, R=CH₃) which as expected was converted by alcoholic hydrochloric acid to 2-nitro-6-methyl-phenanthridine (IX, R=CH₃), identical with an authentic specimen prepared by the method of Morgan and Walls (1932). Since it is highly improbable that (III, R=H) and (III, R=CH₃) nitrate in different positions when the reactions are conducted under the same conditions, it follows that (IX, R=H) is 2-nitro-phenanthridine.

It was difficult to devise any other straightforward synthesis of 3 : 8-diamino-phenanthridine, which had reasonable hope of success. The apparently obvious route through the preparation and degradation of 3 : 8-dinitro-6-methyl-

phenanthridine was in fact unattractive since the cyclisation of 2-acetamido-4'-nitro-diphenyl gives impracticable yields of the corresponding phenanthridine (Morgan and Walls, 1932, 1938). However, 3:8-diamino-6-phenyl-



phenanthridine appeared to be accessible and its synthesis was undertaken, although it was realised that the presence of the aryl substituent would not be advantageous to antiseptic activity. Under carefully controlled conditions 2-amino-diphenyl was nitrated in excess concentrated sulphuric acid by nitric

acid to 2-amino-4:4'-dinitro-diphenyl (X). This method was much more convenient than that of Finzi and Bellavita (1938), who used ethyl nitrate to effect the nitration. These authors stated that by short boiling with acetic anhydride an acetyl derivative melting at 168-9° was formed. On repeating the experiment a product which began to melt at approximately this temperature was obtained, but it was obviously a mixture. By fractional crystallisation from alcohol and aqueous pyridine it was separated into a substance m.p. 175° and another m.p. 195°. Both of these analysed correctly for carbon and hydrogen for an acetamido-dinitro-diphenyl and hence it was thought that the original nitration product was a mixture, in spite of its sharp melting point and homogeneous appearance. But on hydrolysis both yielded the same dinitro-amino-diphenyl, which as a further check was deaminated in each case to 4:4'-dinitro-diphenyl. The matter was finally cleared up when it was realised that the mono-acetyl and di-acetyl derivatives of 2-amino-4:4'-dinitro-diphenyl happened to have very nearly the same percentages of both carbon and hydrogen. Analyses for nitrogen showed that the substance m.p. 195° was the di-acetyl (XII) and the substance m.p. 175° the mono-acetyl (XI) derivative. The facility with which the diacetyl derivative is formed and its stability are remarkable.

The benzoyl derivative (XIII) of the amine, prepared by the usual method, was cyclised by phosphorus oxychloride in nitro-benzene solution at 180° (Morgan and Walls, 1939, 1940) to 3:8-dinitro-6-phenyl-phenanthridine (XIV) in good yield. Because of its slight solubility, the reduction of this substance was troublesome. The usual methods did not give promising results, the products being red intractable gums. From the gum produced by reduction with phenyl-hydrazine in boiling xylene, there was isolated in small yield a bright red substance, which proved to be a nitro amine. This is probably 3-nitro-6-phenyl-8-amino-phenanthridine (XVI) rather than its isomer, since Muller and Zimmermann (1925) have shown that the reduction of a nitro group by phenyl-hydrazine is more difficult when an amino group is attached to the same benzene nucleus. Attempts to effect complete reduction by working at higher temperatures were unsuccessful.

Recourse was then had to catalytic reduction. When a solution of (XIV) in hot dioxane was shaken in an atmosphere of hydrogen in the presence of Raney nickel at atmospheric pressure, the reaction ceased when about 85% of the theoretical amount of hydrogen had been absorbed. The addition of more catalyst did not cause a resumption of hydrogen uptake. The product of the reduction was a thick dark red gum, but by acetylation this was converted to a solid. The purification of this was tedious. Several recrystallisations removed amorphous by-products, but the product was still a mixture. The fractional crystallisation of it from alcohol was rendered long and difficult by the fact that each substance greatly increased the solubility of the other. Eventually a less soluble diacetyl derivative m.p. 296°, and a more soluble triacetyl derivative m.p. 193°, were isolated in a state of purity. On hydrolysis with the concentrated hydrochloric acid both yielded 3:8-diamino-6-phenyl-phenanthridine (XVII).

Dilute solutions of this substance in dioxane and ethyl acetate had a striking green fluorescence, but this was much weaker in alcohol. In concentrated sulphuric acid solution the fluorescence was blue. A 1% solution of the substance in the minimum of N/15 hydrochloric acid was very deep red. On the gradual addition of concentrated hydrochloric acid the colour faded to very pale yellow, and in 10 N solution it was barely perceptible. From more concentrated solutions of the substance in 10 N hydrochloric acid a white hydrochloride was deposited. The intense red colour of the dilute acid solution is due to the formation of a resonating ion, the chief forms of which are shown in (XVIII), by the attachment of a proton to the ring nitrogen atom. In concentrated acid,

protons become attached to the other nitrogen atoms also, eliminating this resonance and thus destroying the colour.

A preliminary test of the antiseptic activity of this substance was made by Dr. H. L. Jensen in the Bacteriology Department of this University, who reported as follows :

"Bacteriostatic effect of the compound was tested towards a strain of *Staphylococcus aureus* used for assay of penicillin. The compound was added from solution in minimum quantity of hydrochloric acid to ordinary meat-extract peptone broth (sterilized separately) in concentrations ranging from 0.1 to 0.001. Duplicate test tubes were inoculated with one drop of young *Staphylococcus aureus* culture dil. 1/10,000 and incubated 48 hours at 37° C.

Result :

	Growth at Concentration Percentage of Compound.						
	0.1	0.05	0.02	0.01	0.005	0.002	0.001
							0 (Control)
After 24-hr. Precipitations		(-)	-	-	-	+	+
After 48-hr. Precipitations		(-)	-	-	+	+	+

"At concentration 0.02% the medium became slightly cloudy and at the two higher concentrations a heavy yellow precipitate was formed.

"3 : 8-Diamino-6-phenyl-phenanthridine thus possesses antiseptic properties, but does not appear highly active, and its apparent protein-coagulating properties would probably militate against its use for many medical purposes."

EXPERIMENTAL.

2 : 2'-Dichloro-5 : 5'-dinitro-benzylidene-aniline (I).

A mixture of 2-chloro-5-nitro-benzaldehyde (1.85 g.) and 2-chloro-5-nitro-aniline (1.7 g.) was kept molten until water was no longer evolved. The product which solidified on cooling was sparingly soluble in the usual solvents but could be recrystallised from cineol or nitrobenzene, from which it separated as pale yellow glistening needles, m.p. 244°.

Found : N, 12.6%. Calculated for $C_{13}H_7O_4N_2Cl_2$: N, 12.4%.

5 : 6-Dihydrophenanthridine (II, R=H).

A solution of phenanthridine (80 g.) in concentrated hydrochloric acid (800 c.c.) was heated with tin (200 g.) under reflux until the tin had almost completely dissolved (about four hours). After cooling, the reaction mixture was made strongly alkaline with sodium hydroxide solution and extracted with ether. Removal of the ether left an oil which rapidly solidified. After washing with a little light petroleum the crude product (76 g.) melted at 122°. The pure substance crystallised from aqueous alcohol or benzene light petroleum mixture in lustrous irregular plates m.p. 123°, which had a beautiful blue fluorescence. It was easily soluble in the usual organic solvents and the solutions showed the same strong blue fluorescence. Solutions in dilute mineral acids were colourless and non-fluorescent.

Found : C, 86.4 ; H, 5.9%. Calculated for $C_{13}H_{11}N$: C, 86.2 ; H, 6.1%.

When shaken with warm 3% potassium permanganate it was rapidly and quantitatively oxidised to phenanthridine.

The *picrate*, prepared in alcohol, crystallised in orange-red needles, which began to darken at 180° but did not melt until 238°.

Found : N, 13.8%. Calculated for $C_{13}H_9O_7N_4$: N, 13.7%.

Nitration of (II, R=H).

The following was a typical experiment. A solution of the base (7.2 g.) in concentrated sulphuric acid (100 c.c.) was nitrated at -3° to -5° by the addition of a mixture of nitric acid (4.4 c.c., sp. gr. 1.5) and concentrated sulphuric acid (10 c.c.). After one hour, the mixture was

poured on to ice when a chocolate coloured product was precipitated. This was mainly amorphous but by fractionation of an alcoholic extract there was finally isolated a bright orange substance (0.2 g.) which crystallised from alcohol in small plates, m.p. 209°.

Found : N, 15.6%. Calculated for $C_{13}H_7O_4N_3$: N, 15.6%.

5-Acetyl-5 : 6-dihydrophenanthridine (III, R=H).

A solution of dihydrophenanthridine in excess acetic anhydride was warmed on the steam bath for twenty minutes and then poured into water. The product crystallised from aqueous alcohol in colourless prismatic needles, m.p. 108°.

Found : C, 80.4 ; H, 5.8%. Calculated for $C_{15}H_{13}ON$: C, 80.7 ; H, 5.8%.

When hydrolysed by boiling with alcoholic hydrochloric acid, it was converted to dihydrophenanthridine.

8-Nitro-5-acetyl-5 : 6-dihydrophenanthridine (V).

A solution of the acetyl derivative (5.5 g.) in acetic acid (7 c.c.) and concentrated sulphuric acid (12 c.c.) was stirred and kept at 0° to 5° whilst it was treated with a mixture of nitric acid (1.3 c.c., sp. gr. 1.5) and acetic acid (3 c.c.). After standing at 0° for one hour longer it was poured into ice water, and the precipitate collected. After many recrystallisations from alcohol, benzene and ethyl acetate in turn, there was finally obtained a pure substance (1.5 g.). It crystallised in orange prisms which melted at 176°.

Found : C, 67.8 ; H, 4.3%. Calculated for $C_{16}H_{12}O_3N_2$: C, 67.2 ; H, 4.4%.

When twice the proportion of nitric acid was used in the above nitration, the product was a thick dark oil. When this was boiled with alcohol (100 c.c.) a yellow crystalline substance (0.7 g.) was gradually deposited. This, which may be (VII), crystallised from benzene alcohol mixture in glistening yellow plates m.p. 218°.

Found : C, 57.2 ; H, 3.4%. Calculated for $C_{15}H_{11}O_3N_3$: C, 57.5 ; H, 3.5%.

8-Nitro-phenanthridine (VI).

A solution of (V ; 1.3 g.) in alcohol (100 c.c.) and concentrated hydrochloric acid (30 c.c.) was refluxed for six hours and then distilled to a small bulk. The residue was basified with ammonia and then extracted with benzene. The oil remaining after evaporating the benzene crystallised when stirred with a little warm methyl alcohol. The pure substance (0.2 g.) crystallised from ethyl alcohol ethyl acetate mixture in glistening orange leaflets m.p. 178°.

Found : C, 69.2 ; H, 3.7%. Calculated for $C_{15}H_8O_2N_2$: C, 69.7 ; H, 3.6%.

It was easily soluble in benzene, moderately in ethyl acetate, but slightly soluble in alcohol.

2-Nitro-5-acetyl-5 : 6-dihydrophenanthridine (VIII, R=H).

Fuming nitric acid (10 c.c., sp. gr. 1.5) was added gradually to a solution of (III, R=H ; 5 g.) in glacial acetic acid (10 c.c.) stirred and cooled in an ice bath. Since no reaction appeared to take place, the reaction mixture was removed from the cooling bath. In a short time, the temperature began to rise rapidly and the product commenced to separate. By suitable cooling the temperature was kept between 20° and 25°. Then after standing at room temperature for thirty minutes ice water was added, and the product collected. The pure substance (4 g.) crystallised from alcohol in pale yellow needles m.p. 181°.

Found : C, 67.1 ; H, 4.5%. Calculated for $C_{16}H_{12}O_3N_2$: C, 67.2 ; H, 4.4%.

2-Nitro-phenanthridine (IX, R=H).

A suspension of (VIII, R=H ; 5 g.) in alcohol (200 c.c.) and concentrated hydrochloric acid (100 c.c.) was refluxed for six hours and then the alcohol was distilled off. The residue was basified with ammonia and the precipitated product collected. After washing well with water,

it was boiled with alcohol (100 c.c.) and filtered from the hot solvent. Recrystallisation from pyridine alcohol mixture afforded pale yellow needles (2 g.) which melted at 263°.

Found: C, 69.8; H, 3.4%. Calculated for $C_{12}H_9O_2N_2$: C, 69.7; H, 3.6%.

It was very sparingly soluble in alcohol, moderately soluble in benzene and easily soluble in pyridine.

6-Methyl-5:6-dihydrophenanthridine (II, R=CH₃).

Reduction of 6-methyl-phenanthridine was accomplished by the method used for the reduction of phenanthridine. The product crystallised from light petroleum in clumps of prisms m.p. 89°, which had a blue fluorescence.

Found: C, 85.9; H, 6.5%. Calculated for $C_{14}H_{13}N$: C, 86.1; H, 6.7%.

Oxidation to 6-methyl-phenanthridine by potassium permanganate was somewhat slower than in the case of dihydrophenanthridine.

The *picrate* separated as sparingly soluble bright red needles when hot alcoholic solutions of its components were mixed. It began to decompose at about 220° but was not completely melted until 240°.

Found: N, 13.4%. Calculated for $C_{20}H_{15}O_7N_4$: N, 13.2%.

5-Acetyl-6-Methyl-5:6-dihydrophenanthridine (III, R=CH₃).

Acetylation in the usual manner gave an acetyl derivative which crystallised from aqueous alcohol in colourless needles m.p. 102°.

Found: C, 80.7; H, 6.2%. Calculated for $C_{16}H_{15}ON$: C, 81.0; H, 6.3%.

2-Nitro-5-acetyl-6-methyl-5:6-dihydrophenanthridine (VIII, R=CH₃).

Nitration of (III, R=CH₃; 9 g.) in acetic acid under the conditions used in the nitration of (III, R=H) gave a product which crystallised from much alcohol in pale yellow plates (9 g.) melting at 204°.

Found: C, 68.3; H, 5.0%. Calculated for $C_{16}H_{14}O_3N_2$: C, 68.1; H, 5.0%.

2-Nitro-6-methyl-phenanthridine (IX, R=CH₃).

A suspension of (VIII, R=CH₃; 8.5 g.) in alcohol (500 c.c.) and concentrated hydrochloric acid (200 c.c.) was refluxed for six hours and then evaporated to a small bulk. After basifying with ammonia it was extracted with benzene. The residue left after removing the benzene was washed with a little alcohol and crystallised from ethyl acetate. It (3.5 g.) separated in long yellow needles which melted at 201°, undepressed by admixture with an authentic specimen, with which it was identical in all respects.

Found: C, 70.4; H, 4.5%. Calculated for $C_{14}H_{10}O_2N_2$: C, 70.6; H, 4.2%.

2-Amino-4:4'-dinitro-diphenyl (X).

The following procedure was developed as the result of many experiments. Departure from the conditions specified leads to poorer yields of less pure product.

A solution of *o*-xenylamine (8.5 g.) in concentrated sulphuric acid (100 c.c.) was cooled to -3° to -5° and vigorously stirred whilst a mixture of nitric acid (5.5 c.c., sp. gr. 1.5) and concentrated sulphuric acid (10 c.c.) was gradually added. The addition, which took about forty-five minutes, was regulated so that the temperature did not rise above -3°. After standing at this temperature for one hour longer the reaction mixture was poured into a large volume of ice and water. The precipitate was collected, washed well with water and then washed by stirring with alcohol (twice, 40 c.c. each time). One recrystallisation from alcohol pyridine mixture gave a pure product (6 g.) as small orange needles m.p. 208°.

Found: C, 55.6; H, 3.4%. Calculated for $C_{12}H_8O_4N_2$: C, 55.6; H, 3.5%.

It was sparingly soluble in the usual organic solvents and insoluble in dilute mineral acids.

4 : 4'-Dinitro-diphenyl.

A solution of (X; 1.3 g.) in concentrated sulphuric acid (5 c.c.) was poured into ice water (60 c.c.) and the finely divided precipitate thus obtained diazotised by the addition of sodium nitrite (0.35 g.) in water (5 c.c.). The reaction was very slow and after eight hours about half of the amine had reacted. The mixture was filtered and the filtrate added to a solution of sodium hypophosphite (3 g.) in water (10 c.c.) at 0°. After standing overnight it was heated to boiling and the product collected. Crystallisation from alcohol and then acetic acid gave pale yellow needles m.p. 231°, undepressed by admixture with an authentic specimen.

Acetylation of (X).

2-Amino-4 : 4'-dinitro-diphenyl (10 g.) was refluxed for five minutes with just sufficient acetic anhydride to dissolve it at the boiling point. After pouring into water, the product was collected, washed, dried and dissolved in boiling alcohol (500 c.c.). The substance which crystallised on cooling was recrystallised from the same volume of alcohol and was then nearly pure (6 g.). When pure it separated from alcohol in nearly colourless irregular flattened needles m.p. 175°.

Analysis showed it to be 2-acetamido-4 : 4'-dinitro-diphenyl (XI).

Found: C, 55.6; H, 3.5; N, 14.3%. Calculated for $C_{14}H_{11}O_5N_3$: C, 55.8; H, 3.6; N, 14.0%.

The first filtrate was evaporated to a small bulk (about 70 c.c.), cooled, and the product which separated collected and dissolved in the second filtrate, which was then evaporated to 50 c.c. The fraction which then crystallised was repeatedly recrystallised from aqueous pyridine, yielding finally the pure *diacetyl derivative* (XII) in glistening plates m.p. 195 (2 g.).

Found: C, 55.4; H, 3.7; N, 12.5%. Calculated for $C_{16}H_{13}O_6N_3$: C, 55.9; H, 3.8; N, 12.3%.

Both substances yielded 2-amino-4 : 4'-dinitro-diphenyl on hydrolysis.

2-Benzamido-4 : 4'-dinitro-diphenyl (XIII).

A solution of the amine (15.6 g.) in dry pyridine (50 c.c.) was treated with benzoyl chloride (7 c.c.) and heated on the steam bath for one hour. Then alcohol (150 c.c.) was added to the hot reaction mixture. The nearly pure product (20 g.) began to crystallise immediately. Recrystallised from alcohol pyridine mixture, it formed very pale yellow needles which melted at 236°. It was sparingly soluble in the usual solvents.

Found: C, 62.8; H, 3.6%. Calculated for $C_{19}H_{13}O_5N_3$: C, 62.8; H, 3.6%.

3 : 8-Dinitro-6-phenyl-phenanthridine (XIV).

A solution of the amide (16 g.) in pure dry nitrobenzene (20 c.c.) and phosphorus oxychloride (10 c.c.) was refluxed in an oil bath at 180°. After twenty hours the slow evolution of hydrogen chloride had ceased. The reaction mixture was poured into excess dilute ammonia and steam distilled to remove nitrobenzene. The product was collected, washed with warm alcohol to remove a soluble amorphous by-product, and then recrystallised from alcohol pyridine mixture. The pure substance (10 g.) separated in very pale yellow needles m.p. 261°. It was sparingly soluble in the usual solvents.

Found: C, 66.2; H, 3.2%. Calculated for $C_{19}H_{11}O_4N_4$: C, 66.1; H, 3.2%.

Reduction by Phenylhydrazine.

When the above phenanthridine (2 g.) and phenylhydrazine (4 g.) in xylene solution (40 c.c.) were refluxed, water soon commenced to separate. After four hours the xylene was distilled off under reduced pressure and the dark red residual oil washed several times with light petroleum. When warmed with alcohol it slowly became partially crystalline and eventually a product (0.3 g.) forming bright red needles m.p. 281.3° was isolated. It is probably (XVI).

Found: C, 72.1; H, 4.2; N, 13.5%. Calculated for $C_{19}H_{13}O_2N_3$: C, 72.4; H, 4.2; N, 13.3%.

Catalytic Reduction of (XIV).

A solution of (XIV; 25 g.) in hot dioxane (1,000 c.c.) was shaken with Raney nickel in an atmosphere of hydrogen at normal pressure. Absorption of hydrogen was rapid at first and when a little more than half of the theoretical amount had been taken up, the solution acquired a strong bright green fluorescence. From this point absorption was slow and stopped completely when about 85% of the theoretical amount had been absorbed. Addition of more catalyst did not result in further action. After filtering off the catalyst, the solvent was removed under reduced pressure and the dark red gum which remained acetylated by warming with excess acetic anhydride on the water bath. The light yellow solid was recrystallised three times from a large volume of aqueous pyridine, twice from much aqueous alcohol, and then fractionally crystallised from alcohol. After a prolonged fractionation two pure substances were isolated.

The less soluble fraction (14 g.), which formed a pale yellow crystalline powder m.p. 296°, was evidently a diacetyl derivative. It was sparingly soluble in the usual solvents.

Found: C, 74.8; H, 5.0; N, 11.4%. Calculated for $C_{23}H_{19}O_2N_3$: C, 74.8; H, 5.2; N, 11.4%.

The more soluble fraction (3.5 g.), a triacetyl derivative, crystallised in pale yellow prisms m.p. 193° with frothing.

Found: N, 10.5%. Calculated for $C_{25}H_{21}O_3N_3$: N, 10.3%.

3:8-Diamino-6-phenyl-phenanthridine (XVII).

When either acetyl derivative was heated with excess concentrated hydrochloric acid, it rapidly dissolved to a yellow solution. In a short time a white hydrochloride began to crystallise out, but refluxing was continued for three hours. On dilution, the precipitate dissolved readily to an intensely red solution from which the product was precipitated by the addition of ammonia (80% yield). Recrystallisation from aqueous alcohol afforded pale yellow irregular prisms melting at 198°.

Found: C, 79.5; H, 5.3; N, 14.6%. Calculated for $C_{19}H_{14}N_4$: C, 80.0; H, 5.3; N, 14.7%.

Dilute solutions of the substance in dioxane or ethyl acetate had a strong bright green fluorescence. In alcohol the fluorescence was much weaker. It dissolved readily in very dilute sulphuric or hydrochloric acid to an intensely red solution, the colour of which faded to pale yellow on the addition of concentrated acid.

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THE PHYSICS OF RUBBING SURFACES.*

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With Plates VIII-XIII and twenty-one text-figures.

PART I.

INTRODUCTION.

In this lecture we shall be dealing with a very old and very unfashionable branch of natural science—friction—and we wish to discuss some of the physical processes that occur when two solids are rubbed together. The title is a comprehensive one but this is in no sense a general summary of the field, and it does not do justice to other workers. There are many obvious gaps, for example no mention is made of frictional electricity. I thought, however, that the most satisfactory way would be to discuss certain aspects of the subject from my own point of view, and to deal with some of the work of my associates and colleagues. The more recent work was done under the Council for Scientific and Industrial Research in the Chemistry Department of the University of Melbourne, and the earlier work in Cambridge. At the outset I must offer an apology. For the past five years we have been concerned almost entirely with war problems and the basic work we have been able to do has been fragmentary and fitted into odd corners. For the same reason the pressure of immediate work has made it impossible to give the proper thought and preparation that the Liversidge Lecture warrants.

It would be interesting to attempt a lecture on the *chemistry* of rubbing surfaces, but unfortunately our information about this is very scanty. Although we know a great deal about the influence of heat, of light, and of electricity in stimulating molecules to react, we still know comparatively little about the influence of mechanical forces on reactivity and of the effects produced when we seize a molecule by the head and the heels and tear it in half. We shall confine our attention to some of the physical processes that occur when one solid slides over another. There is a resistance to motion which we call friction. What is the mechanism of that frictional force, and from the point of view of a molecule sitting on the surface, what is really happening? We may ask a few simple questions and then endeavour to answer them by direct experiment. To begin with we wish to ask three questions: (i) what is the real area of contact between the solids? (ii) What is the surface temperature of the rubbing solids? (iii) What is the nature of the surface damage?

THE REAL AREA OF CONTACT BETWEEN SOLID SURFACES.

It is, of course, a very difficult matter to prepare surfaces which are really flat. Even on carefully polished surfaces hills and valleys which are large compared with the dimensions of a molecule will still be present. The upper

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surface will be supported on these irregularities and large areas of the surfaces will be separated by a distance which is great compared with the dimensions of a molecule. We do not know very much about the size of these small irregularities nor the degree of flatness of the surfaces. Optical methods cannot reveal irregularities much smaller than one-half to one-tenth of a wave length of light. Although the techniques of grinding and polishing have advanced in the past few years, it is still a difficult matter to prepare surfaces of appreciable size which are flat to within one or two thousand angstroms. Since the range of molecular attraction is only a few angstroms, we may expect that the area of intimate contact, that is the area over which the surfaces are within molecular range, will, even for very carefully prepared surfaces, be quite small. A new and powerful method for studying surface irregularities and surface structure is the electron microscope, and recent stereoscopic pictures taken by Heidernich and Matheson (1944) show in some detail small scratches *ca.* 250 Å. deep on polished metal surfaces.

In general the surfaces used in engineering practice are less flat and the surface irregularities present on them are, in terms of molecular dimensions, enormous. These irregularities may be seen by cutting a section at right angles to the surface and examining it with high power microscope, but a more revealing method is to cut a section at an oblique angle to the surface. This has the advantage that it magnifies the irregularities in the vertical direction and leaves the horizontal magnification unchanged. Taper sections prepared in this way by Mr. Moore which show some characteristic contours of surfaces finely machined and also ground with abrasives of varying degrees of fineness are given in Plate VIII, Figs. 1-5. It is seen (Fig. 5) that even with the finest abrasive the surface irregularities are of the order of 0.1μ , i.e. 10^{-5} cm.

If the surfaces are polished the effect is to cause the summits of the peaks to flow into the valleys so that the contour resembles rolling downs rather than rugged alpine peaks. But again the surfaces will touch on the summits of the hills and the area of intimate contact will be small.

Some knowledge of the real area of contact between solid surfaces is essential for our purpose and its determination is a matter of some experimental difficulty. Fortunately, an approximate estimate of it in the case of metals can be made by measuring the electrical conductance across the surface of the metals when they are in contact.

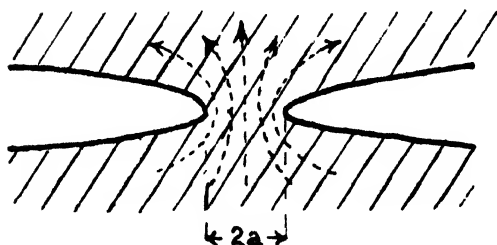


Fig. 1.—The current flow through a constriction of radius a in a metal conductor. The behaviour is similar if two metal surfaces make electrical contact over an irregularity of radius a . The electrical conductance Λ of such a junction is given by $\Lambda = 2a\lambda$.

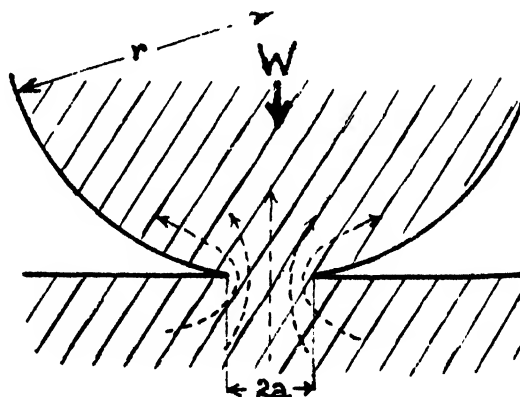


Fig. 2.—The deformation of a spherical surface resting on a hard (undeformable) plane surface. The current flow and electrical conductance are similar to those described in Fig. 1.

In the simple case of metal surfaces which make electrical contact over a surface irregularity of radius a (see Fig. 1) it can be shown (Maxwell, 1873; Holm, 1929; Bowden and Tabor, 1939) that the conductance Λ is given by

$$\Lambda = 2a\lambda \dots\dots\dots (1)$$

when λ = the specific conductivity of the metal. A measurement of the conductance will therefore enable us to estimate the area of contact.

Variation of Area of Contact with Load.

Hertz (1881), in his classical paper on the elastic deformation of solid surfaces, calculated how the area of contact between curved surfaces should depend upon the load. He showed that, if *elastic* deformation is assumed, the theoretical radius of contact a between a spherical surface resting on a plane surface of the same material (see Fig. 2) is given by

$$a = \text{const.} \left(\frac{Wr}{E} \right)^{\frac{1}{3}} \dots\dots\dots (2)$$

where W is the load between the surfaces, r is the radius of curvature of the spherical surface and E is Young's Modulus.

From equations (1) and (2)

$$\Lambda = \text{const.} W^{\frac{1}{3}} \dots\dots\dots (3)$$

so that if we assume elastic deformation of the metals in the region of contact the conductance should be proportional to the *cube root* of the load. There is, however, another possibility. We may consider that the metal in the region of contact will flow *plastically* under the applied load until the cross section of the contact is sufficient to support the load.

In this case

$$W = \pi a^2 f \dots\dots\dots (4)$$

where f is the maximum pressure the metal can withstand without flowing. Combining this with equation (1) it follows that

$$\Lambda = \text{const.} W^{\frac{1}{2}} \dots\dots\dots (5)$$

i.e., the electrical conductance should be proportional to the *square root* of the load.

Some experiments were carried out by Dr. Tabor to investigate this point and results obtained for a number of different metals in contact are shown in Figs. 3 and 4. In these experiments two crossed cylinders were used, since geometrically this is the same as a spherical surface resting on a flat one and it is more convenient experimentally. It is clear that the conductance varies in an orderly manner with the applied load. Moreover, an examination of the slope of the lines (see Fig. 4) shows that the conductance is proportional to the *square root* of the load, i.e. equation (5) is obeyed, and hence the deformation of the surfaces in the region of contact is mainly *plastic*.

Some actual values of the area of contact between cylinders of steel and between cylinders of silver at different loads are given in Table 1.

TABLE 1.
Area of Contact between Cylinders of Steel and Silver at Various Loads.

Load. Kg.	Area of Contact cm. ² (From Electrical Conductance.)	
	Steel.	Silver.
0.5	—	0.0002
1	0.00013	—
5	0.00061	0.002
50	0.0045	0.018
500	0.042	0.15

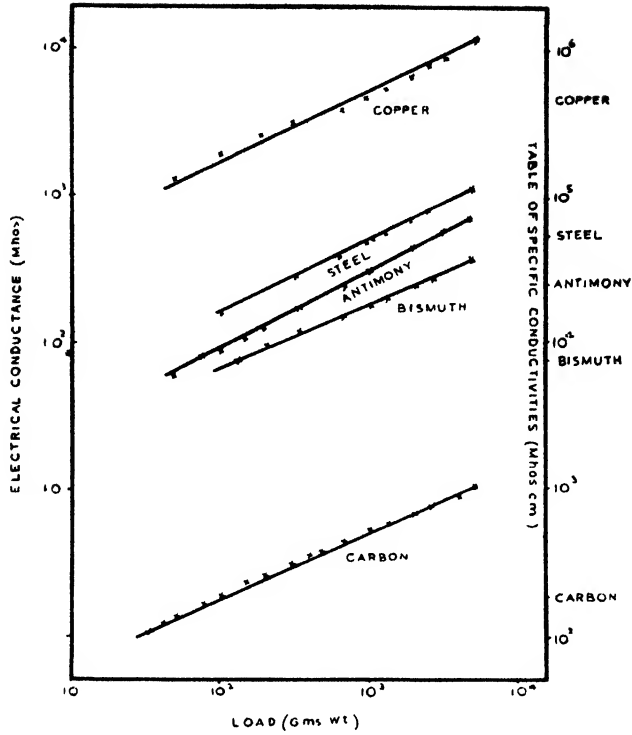


Fig. 3.—The variation of electrical conductance with load for crossed cylinders of various materials. The conductance varies in an orderly manner with load and the position of the curve for each material is in the same order as the specific conductivity of the material.

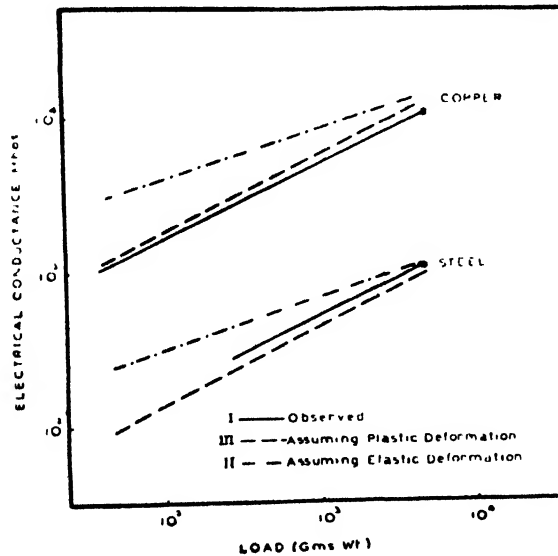


Fig. 4.—Variation of electrical conductance with load for crossed cylinders of copper and steel. The broken lines are calculated assuming plastic and elastic deformation. The observed values show that the deformation is essentially plastic.

Area of Contact between "Flat" Surfaces.

It is interesting to compare the conductance across flat surfaces with that across curved surfaces at the same load, and Fig. 5 shows such a comparison.

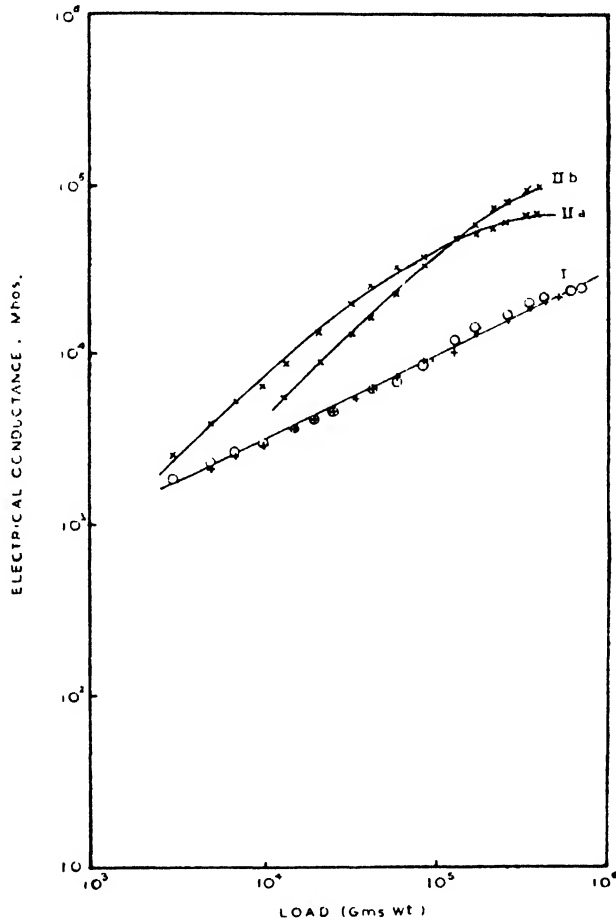


Fig. 5.—Variation of electrical conductance with load for steel surfaces. Curve I refers to curved surfaces, Curve II (a) to flats 0.8 sq. cm. in area, Curve II (b) to flats 20 sq. cm. in area.

Curve I is for curved surfaces of steel, Curve II (a) for flat steel surfaces 0.8 sq. cm. in area, Curve II (b) for similar surfaces 20 sq. cm. in area. The surfaces were flat to a few fringes. The values for flat surfaces do not lie on a straight line but it is clear that the values of the conductance are not very different from those observed with curved surfaces. The possible area of contact between the flat surfaces is of course enormously greater than that of the curved, but the conductance is of the same order of magnitude. At a load of 5 kg., for example, the area of contact between the curved surfaces is $ca. 6 \times 10^{-4}$ sq. cm. If nearly all the surface of the 21 cm. flat were in contact the area of contact would be $ca. 30,000$ times as great and the conductance would be correspondingly increased. Experiment shows, in fact, that it is only twice as great. It is thus clear that only a very small fraction of the flat surfaces can be in intimate contact. It will also be noted that the conductance of both sizes of flats is almost the same although their apparent areas stand in the ratio of 30 : 1. We can conclude that the conductance is independent of the apparent area of the surfaces. It

depends mainly on the load. Experiments also showed that the conductance was little influenced by the degree of roughness of the surfaces. The surface of the steel cylinders was rubbed with a coarse file so that it was as rough as possible and the conductance was compared with that of a finely ground surface. No appreciable difference between the two was observed.

It is clear from these simple experiments that the area of intimate contact between solid surfaces is very small indeed. It varies with the pressure, but for flat steel surfaces it may be less than one-tenth thousandth of the apparent area. The real area of contact is not greatly affected by the size of the surfaces nor by the shape and the degree of roughness of the surface. It depends mainly on the pressure.

The general behaviour is consistent with the view that the surfaces are held apart by small irregularities. This means that even with lightly loaded surfaces the local pressure at these small points of contact is very high and may be sufficiently great to cause steel to flow plastically. Although the stresses will cause elastic deformation of the metal in the vicinity of the points of contact the experiments suggest that the summits of irregularities on which the bodies are supported flow plastically and are crushed down until their cross section is sufficient to enable them to support the applied load.

The fact that the real area of contact is so small has important practical implications. Even when loads of only a few hundred grammes are applied to the surfaces the local pressure between them may be sufficiently great to cause the flow of metal. When large flat surfaces are used it does not mean that the real pressure is much less, but merely that the points of contact are more widely distributed.

As we shall see later, this intense pressure may cause an actual welding together at the tiny points of contact and so produce small metallic junctions between the surfaces. The pressure between the surfaces in the regions where contact occurs is determined primarily by the flow pressure of the metal itself and is only influenced to a secondary degree by the shape and size of the surfaces and by the load which is applied.

It is interesting to note that even when the surfaces are lubricated with a boundary film of a good lubricant, similar conditions hold. The load will again be carried by the surface irregularities and even for light loads the local pressure on the lubricant film will be very high. In the case of mild steel, for example, it will be $\sim 10^4$ kg. cm.². Unless the lubricant molecule possesses an active group capable of attaching it firmly to the surface the local high pressure will force it from underneath the points of contact. In this sense all good lubricants must act as extreme pressure lubricants.

We would now like to consider in some detail the physical processes that occur when we set these solids in motion and cause one to slide over the other. We find that an appreciable tangential force is necessary to start them moving (static friction) or to keep them sliding (kinetic friction). This frictional resistance occurs, of course, over the small localized regions where the solids are actually in contact, and we will enquire into its mechanism.

THE SURFACE TEMPERATURE OF RUBBING SOLIDS.

The energy lost during sliding is dissipated mainly in the form of heat and the first query is, what will be the temperature of the surfaces? Quite primitive calculations of the amount of heat which is liberated and of the rate at which it is conducted away suggest that the temperature rise of the surface layers may be high. If we endeavour to measure this by embedding thermocouples in the solids near the surface we find that the rise is very small, but this is mainly because we cannot get close enough to the surface. An obvious method is to use the surfaces themselves as a thermometer. This can be done by making

them of two different metals, and using the rubbing contact itself as a thermocouple. A measurement of the electromotive force generated on sliding them provides a record of the surface temperature. It is apparent that the electrical contact and the friction occur at the same points where the surfaces touch so that the measurement gives information about the temperature of the surface layer of the metal where they are rubbing.

Such measurements confirm in a very striking way the existence of local high temperatures at the points of contact of the rubbing surfaces. As would be expected, the temperatures reached depend upon the load, the speed of sliding and the thermal conductivity of the metals. Also the temperatures fluctuate very rapidly during sliding and it is necessary to use an instrument of high frequency such as a cathode ray tube or high frequency galvanometer in order to record them. Fig. 6 shows the maximum temperature reached when small cylinders of gallium, Wood's alloy, lead, and constantan are slid on a steel surface.

It will be seen that with the lower melting metals we readily reach their melting point and the temperature does not rise above this. With constantan, temperatures of the order of $1000^{\circ}\text{C}.$ are reached. These temperatures are

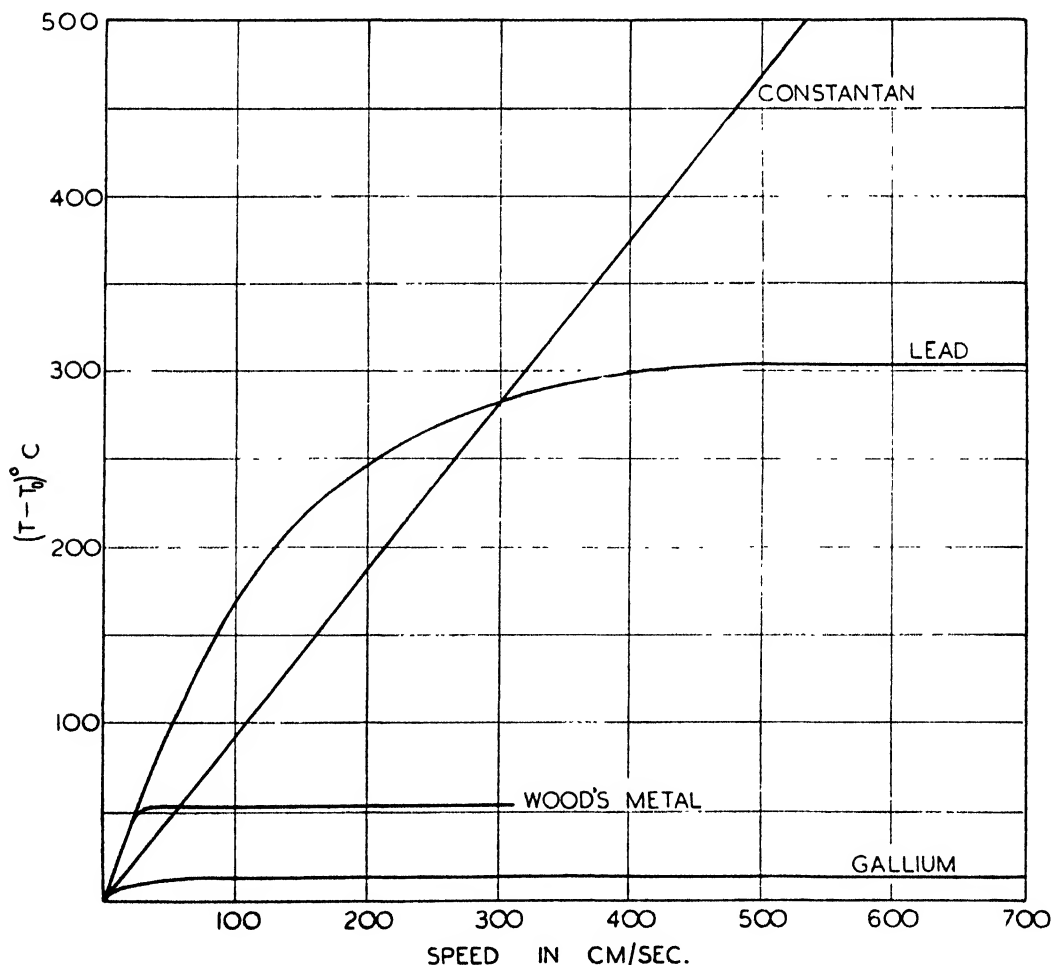


Fig. 6.—Maximum temperatures reached when small cylinders of gallium, Wood's metal, lead and constantan are slid on a steel surface. The temperature cannot exceed the melting point of the metal.

confined to the very thin surface layer and the mass of the metal appears to be quite cool. The rapid and intense nature of the temperature fluctuations is shown strikingly in the cathode ray trace recently taken by Mr. Stone and Mr. Tudor (Fig. 7). It will be seen that the very high temperature flashes of 1000°C . may last only for a few ten-thousandths of a second.

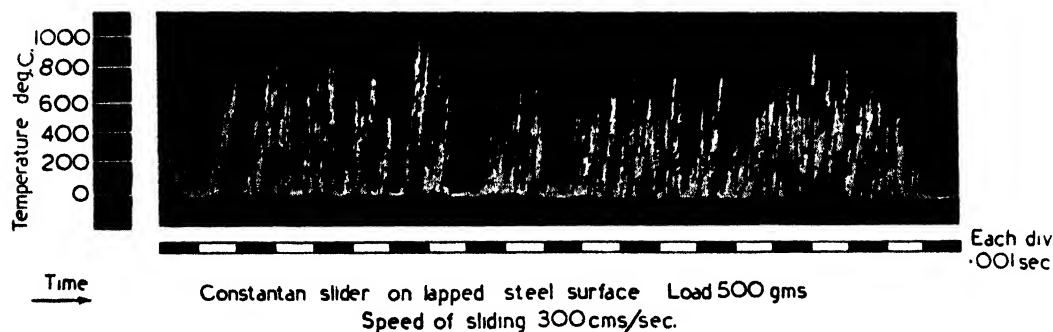


Fig. 7.—Cathode ray trace of thermal emf. developed between a constantan slider on a lapped steel surface. The temperature flashes are extremely high and of very short duration.

It is interesting to note that if the surfaces are flooded with water the local high temperatures may still occur. If the surfaces are lubricated with a boundary film of good lubricant the surface temperatures are greatly reduced but the experiments show that localized metallic contact may still occur through the film and the surface temperature at the summits of the surface irregularities may still be sufficiently high to cause volatilization and decomposition of the lubricant film.

The influence of the thermal conductivity of the metals on the surface temperature is shown in Fig. 8. It will be seen that, with the metals of lower thermal conductivity such as bismuth, the temperature rise is considerably greater.

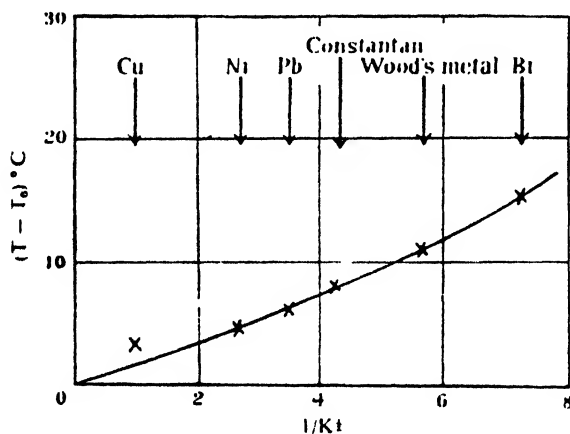


Fig. 8.—Temperature rise of rubbing surfaces as a function of their thermal conductivity K (load 32 g., velocity 20 cm./sec.).

Visual Observation of Hot Spots.

We should expect that these high temperatures would be reached very much more readily on glass and other non-conducting solids. Unfortunately,

the thermocouple method cannot be used with these solids but recently Mr. Stone has shown the existence of the hot spots by visual means. If polished surfaces of glass or quartz are used and the apparatus so arranged that a clear image of the rubbing surfaces can be seen it is found that when sliding starts a number of tiny stars of light appear at the interface between the rubbing surfaces. The points of light are reddish in colour at low speeds and become whiter and brighter as the speed or the load is increased. It is clear that they correspond to small hot spots on the surface and their position shifts continuously as sliding proceeds. They can be recorded photographically. The method is not quantitative but, by making one of the surfaces of metal and using alloys of different melting points, it is possible to fix approximately the temperature at which hot spots first become visible. Experiments suggest that this temperature is about 500°C . These hot spots may occur at very low sliding speeds. For example, with constantan sliding on glass under a load of 1 kg. hot spots appear when the sliding speed is as low as 30 cm. per sec. An example of the photographic method of recording the light from the hot spots is shown in Plate IX, Fig. 1. The surfaces (steel on glass) are allowed to run continuously for two minutes in a circular track so that a cumulative exposure of the hot spots occurs. The circles of decreasing radius mean decreasing sliding speed. The lowest speed at which the hot spots are recorded under the conditions of the experiment is 70 cm./sec.

The fact that these high temperatures occur so readily is of some interest and it is suggested that they may play an important part in a number of processes associated with the rubbing of solids. Before considering its bearing on friction we may enquire what part it plays in the polishing of solids.

POLISHING AND THE SURFACE FLOW OF SOLIDS.

The usual method of polishing surfaces is to rub them together with a fine powder between them. By this process a rough surface having visible surface irregularities is changed into one where the irregularities are invisible. If the surface gives specular reflection the height of these irregularities will be less than half a wave length of visible light. The classical work on polishing is that of Sir George Beilby (1921), who showed that the top layer of the polished solid is different in structure from that of the underlying material. It has lost its obvious crystalline properties and has apparently flowed over the surface, bridging the chasms and filling up the irregularities in it. The mechanism of the process has been a subject of discussion for many years. Newton, Herschel and Rayleigh considered that polishing was essentially due to abrasion. Beilby's view is that it is a surface tension effect—that when the polisher tears off the surface atoms the layer below this “retains its mobility for an instant and before solidification is smoothed over by the action of surface tension forces”. As we have seen, however, the frictional heat generated at the rubbing surfaces may easily raise the temperature to a high value and this suggests that the local thermal softening or actual melting may play an important part in the polishing process.

The action of a typical polisher may be represented diagrammatically in Fig. 9. The polishing particles of rouge or alumina are embedded in a block of pitch and rubbed on the specimen in the presence of a liquid such as water.

At the points of rubbing contact between the polishing powder and the specimen, hot spots will occur which will cause a local surface softening or melting of the specimen. The melted or softened solid would be smeared over the surface and would quickly solidify to form the Beilby layer.

We may perform a simple experiment to test this hypothesis. If polishing is due primarily to a mechanical abrasion and wearing away of the specimen we may expect the relative *hardness* of the specimen and of the polisher to be of major importance. If, however, it is due to surface melting it is the

relative melting points which will be the determining factor. If the polisher melts or softens at a *lower* temperature than the specimen it will melt or flow first and will have comparatively little effect on the specimen.

The result of rubbing Wood's metal (M.P. 75°) with a camphor block (M.P. 178° C.) is shown in Plate IX, Fig. 2. Although the Wood's metal (hardness *ca.* 2) is very much harder than the camphor, it melts at a lower temperature and it will be seen that surface flow and polishing of the alloy occurs. On the other hand camphor will not polish tin (M.P. 232° C.), lead, white metal or zinc, which melt at a higher temperature. A polisher using a powder of oxamide (M.P. 417°) will readily cause flow of all these metals but does not produce any effect on speculum metal (M.P. 745°) (see Plate IX, Fig. 3) or copper (M.P. 1083°) which melt at temperatures well above 417° C. Lead oxide (M.P. 888°) will polish speculum metal and all metals melting below it, but has little effect on nickel and molybdenum, which melt above it. These in turn are readily polished by the high-melting oxides such as chromic oxide, stannic oxide, etc.

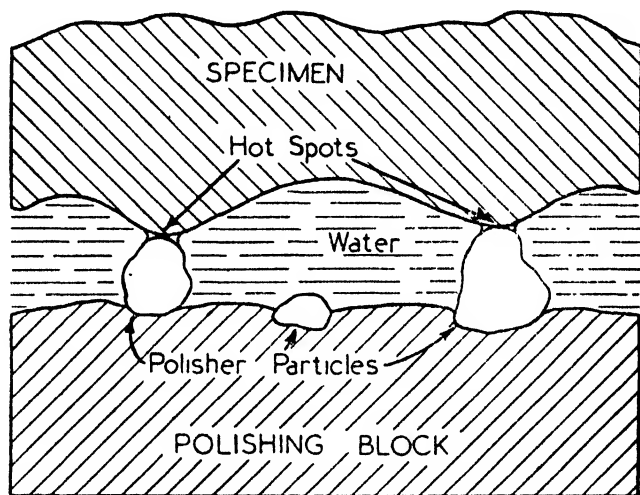


Fig. 9.—Diagrammatic representation of a typical polisher.

Similar results are obtained with glasses, quartz and some non-metallic crystals; calcite, for example (Plate IX, Fig. 4), shows no flow on cuprous oxide which melts a little below it, but is readily polished by zinc oxide which melts above it.

It is well known that the mechanical strength of many metals and solids falls to a very low value at temperatures well below the melting point. The rounding of sharp metal crystals and the low value of tensile strength, hardness, etc., at these temperatures show that metals may lose their rigidity and resistance to shear at comparatively low temperatures. For such solids, surface flow would be expected to take place at temperatures well below the melting point and experiment shows that, in many cases (e.g. gold) this can occur. The rate of flow and polish is, however, very much less and may take hours, instead of the few minutes required by a high melting polisher.

The experiments provide strong evidence, not only that high local temperatures occur, but that they play a large part in the process of polishing. In many cases the frictional heat will raise the temperature to a sufficiently high value to cause a real melting of the solid at the points of sliding contact. The molten solid will flow or will be smeared on to cooler areas, and will very quickly solidify to form the Beilby layer. Polishing under these conditions is rapid.

If the sliding is gentle or the melting point of the polisher is low, the surface of the solid may not reach the temperature of melting. Polish and surface flow may still occur under these conditions, provided the temperature reaches a point at which the mechanical strength of the solid is sufficiently low for it to yield under the applied stress or under surface tension forces. Polishing under these conditions is a slow process.

The relative hardness of solid and polisher as normally measured at room temperature is comparatively unimportant. This is shown clearly in the case of Wood's alloy and tin on camphor, or speculum metal and nickel on lead oxide. The harder metal of low melting point is polished, while the softer metal of higher melting point hardly flows at all. Similarly zinc oxide which is comparatively soft (Mohs' hardness 4) readily polishes quartz (Mohs' hardness 7). The amount of surface flow is governed, not by the properties of the solids at room temperature, but by their relative mechanical properties at the high temperature of the sliding surfaces.

THE MECHANISM OF SLIDING ON ICE AND SNOW.

Another phenomenon where surface melting may play a part is in the sliding of solids on ice and snow—in skating or skiing. It is well known that the friction under these conditions may be remarkably low ($\mu = \text{ca. } 0.03$). The suggestion has often been made that in skating or skiing the surfaces are lubricated by a layer of water formed by pressure-melting (e.g., Reynolds, 1901), but few experiments have been made to support or to disprove the suggestion.

Experience shows that skis slide quite readily on snow at -20°C . Calculations of the pressure necessary to cause melting at this low temperature suggest that it is unlikely that they would be attained. On the other hand calculations of the amount of heat liberated by frictional heating as the ski moves forward a small distance show that it is sufficient to warm up the snow and to melt an appreciable water layer. Some experiments were carried out at the Jungfraujoch Research Station in Switzerland, to determine whether a water layer is formed at all, and if so, whether it is due to pressure melting or to frictional heating. Measurements of the electrical conductivity between metallic electrodes on the bottom surface of miniature ski sliding on salty ice indicated that at low temperatures the surface melting occurred only at localized areas but at temperatures near 0°C . a continuous water film was formed.

The effect of temperature on the friction of different solids sliding on ice surfaces is shown in Fig. 10. It will be seen that the friction increases markedly as the temperature falls and at a temperature of -140°C . it is some five or six times as great as it is at 0°C . The value for the coefficient of friction ($\mu_k = 0.1$) at these low temperatures is of the same order of magnitude as that observed on other crystalline solids such as calcite. The large influence of temperature on the friction of ice is in marked contrast to the behaviour of most other solids where temperature has only a small influence. It emphasizes the anomalous behaviour of ice and supports the view that the low friction is due to a lubricating water layer. As the temperature falls it becomes increasingly difficult for a water layer to be formed and the friction rises.

It is of particular interest to determine the influence that the thermal conductivity of the ski has on the friction at low temperatures. If sufficient pressure is applied to the ice to lower the melting point to the actual temperature of the ice, it is, of course, capable of melting. An appreciable quantity cannot melt, however, unless heat is supplied from some source at a temperature higher than the pressure melting point equilibrium. Both the heat capacity of the ice and its thermal conductivity are small and this heat can most readily be supplied from some outside source. If the temperature of the atmosphere is higher than either of the ice surfaces, it could be supplied by conduction from the air.

Under these conditions we should expect that the friction of a good thermal conductor would be less than that of a bad one. The friction of a brass ski on cold ice should be *less* than that of an ebonite one.

If, however, the lubricating film is formed by frictional heating, the converse will be true. The frictional heat is liberated at the interface between the sliding surfaces, and if the ski is a good thermal conductor, the heat will be carried away rapidly and less will be available for surface melting. On this view the friction of a brass ski on cold ice should be *greater* than that of an ebonite one. Fig. 10 shows the results obtained using a miniature ski of brass and of ebonite.

At temperatures near 0°C . the frictions of both skis were the same. At lower temperatures, however, the results showed that the friction of the brass was considerably greater than that of the ebonite. The lower the temperature the more pronounced this difference usually became. These results provide evidence that the frictional heating plays an important part in the formation of the water film.

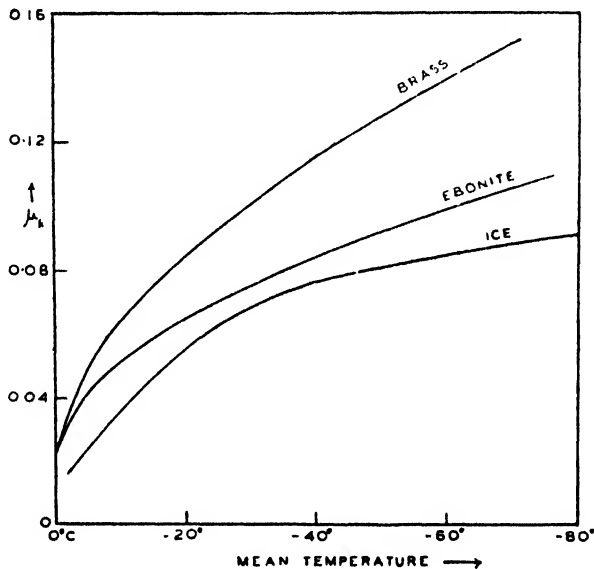


Fig. 10.—Effect of temperature on the friction of brass, ebonite and ice sliding on ice. The friction increases markedly as the temperature falls and is lower for the slider possessing the lower thermal conductivity.

The observations have an interesting bearing on sledging and skiing. No quantitative measurements of the friction of sledges seem to have been published, but there is general agreement that the friction increases at low temperatures. Many arctic explorers (Wright, 1924, p. 44 ; J. M. Scott, 1933, p. 273 ; Cherry-Garrard, 1922, pp. 456-7) have recorded that at very low temperatures, -30 to -40°C ., the friction between the snow and the runners became so great that the sensation was that of pulling a sledge over sand. Wright, summarizing the conclusions of the Scott Polar Expedition of 1911-13, says :

"Quite apart from any question of the hardness of the snow, however, the surface temperature has an important influence. Our opinion was that the friction decreased steadily as the temperature rose above zero Fahrenheit (-18°C .), the presence of brilliant sunlight having an effect, which was more than a psychological one, on the speed of advance. Below zero Fahrenheit (-18°C .) the friction seemed to increase progressively as the temperature fell, as if a greater and greater proportion of the friction were due to relative move-

ment between the snow grains and less to sliding friction between the runner and snow." This steady increase in friction as the temperature of the ice or snow falls is clearly shown in Fig. 10. The effect is less marked at very low temperatures, and it is probable that below -40°C . very little surface melting occurs under these conditions.

The influence of the thermal conductivity of the sliding body on the friction, shown in Fig. 10, is also borne out by practical experience. It will be seen from this figure that at low temperatures the friction of a good thermal conductor is considerably greater than that of a poor one. Nansen (1898, pp. 445-6) compared two sledges, one having nickel plated runners and the other maple runners. The temperature was low—the actual value is not given but the mean temperature during that month was -36.8°C . (-34.2°F .). He found that the friction of the metal was higher: "The difference was so great that it was at least half as hard again to draw a sledge on the nickel runners as on the tarred maple runners."

The thermal conductivity is also important in skiing. Nowadays most skis are fitted with brass or steel edges, although sometimes vulcanite or composition edges are used. The friction measurements show that the latter should be faster at low temperatures. If metal must be used, one of low thermal conductivity such as German silver or constantan should be better.

THE SURFACE DAMAGE OF SLIDING METALS.

Returning again to the sliding of metallic surfaces, there are, as we have seen, two major experimental observations. First that the area of contact between them is very small so that the pressure in the local regions of contact is very high and is sufficient to cause plastic flow of the metal, and secondly that at sliding speeds frequently used in practice the surface temperatures may rise to very high values. The third point we need to investigate is the type of interaction between the moving surfaces and the physical changes which occur in them during sliding. Careful examination shows that some surface damage always occurs even with lightly loaded, well lubricated surfaces. The nature of the damage depends upon the combination of metals which is used. Plate IX, Fig. 5, shows the tracks formed (i) on a softer metal when a hard one slides over it, (ii) on a harder metal when a softer one slides over it, (iii) when similar metals are used. In these experiments a heavy load was used and the surfaces were unlubricated so that the effect could be seen more clearly. It will be seen that in (i) a ploughing out and tearing of the softer metal has occurred; in (ii) the harder surface is comparatively little damaged but the softer metal has welded on to it and remains adhering to the surface. With similar metals (iii), which are homogeneous, the damage is more profound and it is this combination which always gives the highest friction. (It should be emphasized that in these experiments and in the ones described below the sliding speed was very slow (a few millimetres per second), so that the temperature rise is inappreciable.)

Highly magnified taper sections made by Mr. Moore which represent a cross section of these three types of tracks are shown in Plate X, Figs. 1-4. Plate X, Fig. 1 shows a track characteristic of type (i) made on a steel surface.¹ The localized nature of the damage is at once apparent. A considerable area of the surface is unchanged. At a number of points, however, penetration, ploughing and tearing of the metal have occurred. The depth of these torn channels varies from considerably less than 10^{-4} cm. to about 10^{-3} cm. At other points on the surface the metal is raised above its former level. Some of

¹ It is interesting to note that when steel is slid on steel the frictional behaviour and the surface damage are characteristic of *dissimilar* metals. This is because steel is a non-homogeneous alloy. If pure iron or a homogeneous steel alloy (e.g., stainless steel) is used, the friction is considerably higher and the behaviour is characteristic of type (iii).

this torn metal comes from the lower surface and some of it is probably left behind by the slider.

If the upper surface is of a softer metal, this ploughing out is not observed. Instead, small fragments of the softer metal are left welded on the harder one. Characteristic welded junctions of this type, formed when copper (hardness 60 B.H.N.) is slid on mild steel at a low speed are shown in Plate X, Fig. 2. The greater part of the steel surface was undamaged, and isolated fragments of copper were left adhering to the steel and distributed over it. For these junctions the shearing has occurred in the copper itself. In other cases, for example the hollows and pits, *C*, shown in Plate X, Fig. 2, the copper has *plucked out* small fragments of the steel. Microphotographs of the copper steel junctions at higher magnifications are shown in Plate X, Fig. 3. The white portion of the steel is ferrite, the dark portion is pearlite, and *A* is a copper fragment ca. $5 \cdot 10^{-3}$ cm. wide and ca. 10^{-3} cm. high. It is clear that the copper is welded on to the steel and that the junction has sheared in the copper itself. It is seen that the forces which sheared through the copper have also caused appreciable deformation of the underlying steel, and have actually raised portions of the steel above the general level of the steel surface. Over a large portion of the surface, however, there is no apparent change in the surface.

A section of the track formed when similar metals slide (copper on copper) is shown in Plate X, Fig. 4. In this case the friction is higher, $\mu \sim 1$ instead of $\mu \sim 0.7-0.8$ in Plate X, Figs. 1 and 2, and the damage is great. The ploughing and tearing are very evident. It is interesting to note that the work hardening and deformation of the metal occur to a considerable depth below the actual track.

The Chemical Detection of Metal picked up during Sliding.

When the surfaces are lubricated the metallic interchange between the surfaces is very greatly reduced so that its detection, even by the taper section method, is very difficult. It may, however, be detected by a technique described by Hunter, Churchill and Mears (1942), and Mr. Moore has applied this method to the examination of the frictional tracks. A gelatine coated paper is soaked in a suitable electrolyte and pressed while still wet against the surface to be examined. A small current is passed between the paper and the metal so that the metallic ions pass into the gelatine. As they are prevented from diffusing by the gelatine the ions concentrate in a pattern corresponding to their distribution on the metal surface. By means of a suitable spot reagent the distribution of ions in the gelatine can be shown up. The results obtained with copper sliding on steel are shown in Fig. 11. The copper slider has passed over the steel surface once. The track widths are magnified 15 times.

It will be seen that the pick-up of the copper on the polished surface is fairly random with a slight tendency to be arranged in lines parallel to the track. These would correspond to high spots on the copper contact as it is worn down.

However, with the lapped surface the lapping scratches which are across the tracks have influenced the pick-up of copper resulting in a number of regions of high copper concentration stretching right across the track and parallel to the lapping scratches. Under lubricated sliding, the same effects are noted but to a much smaller degree. It is apparent from these pictures that marked pick-up of copper can occur under both clean and lubricated conditions and that it occurs more readily at the high spots of either of the two sliding surfaces.

This method is extremely sensitive and it is probable that the amount of copper on the surface of the lubricated steel is less than a millionth of a gramme.

A still more sensitive method is to use a radio-active metal as one of the sliders and detect the presence of any picked-up metal by a Geiger counter. By this method quantities of the order of 10^{-9} to 10^{-10} grammes can be detected.

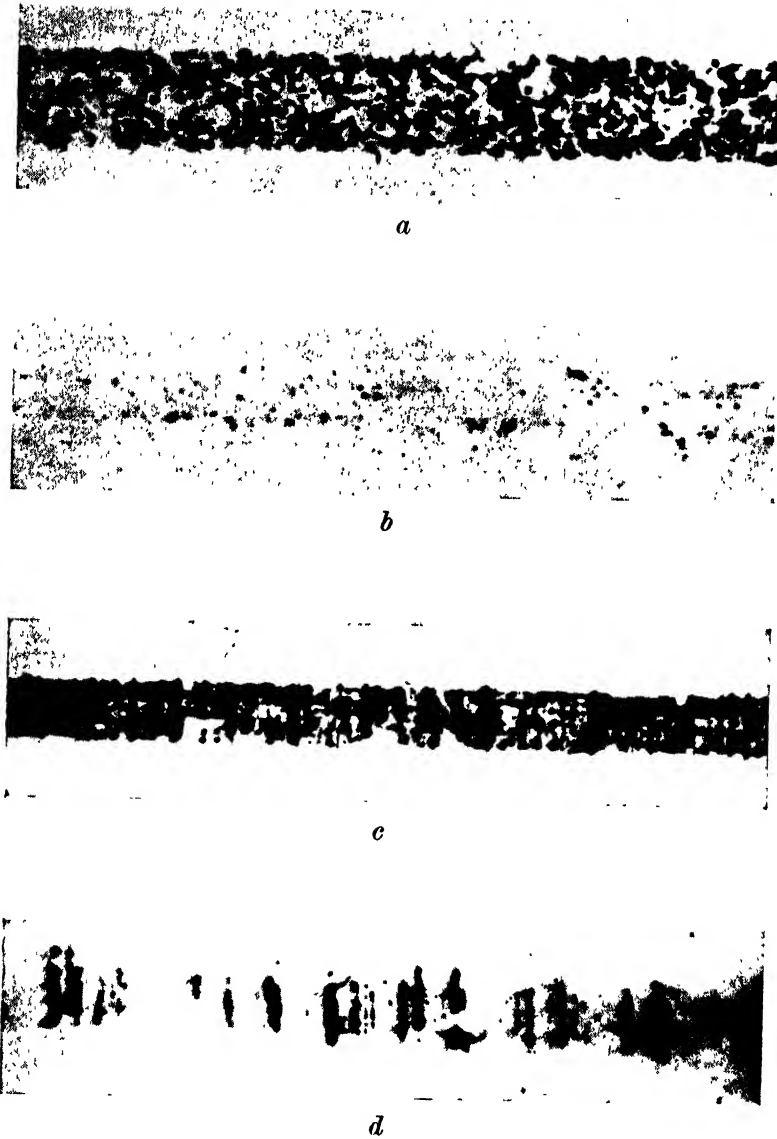


Fig. 11.—Electrographic surface analysis: magnified chemical patterns showing distribution of copper adhering to a steel surface after traversing the steel surface once. Magnification $\times 15$

- (a) Polished steel surface, unlubricated. This represents the same type of surface as Plate X, Fig. 2, and shows very marked pick-up.
- (b) Polished steel surface, lubricated. Although the pick-up is very much reduced it is still apparent.
- (c) Lapped steel surface, unlubricated. The pick-up is very heavy.
- (d) Lapped steel surface, lubricated. The pick-up is less but well marked. In both (c) and (d) the pick-up is concentrated in regions corresponding to the lapping scratches in the steel surface.

Experiments using this method were begun by the writer when in Cambridge in 1938, but they were interrupted by the war. Recently, however, and independently, workers at the Massachusetts Institute of Technology in America (Sakmann, Burwell and Irvine, 1944) have applied the method to steel and other metals sliding on radio-active copper beryllium. They have confirmed in a very beautiful way the observations that metal is picked up through the lubricant layer even with light loads, and have measured the amount.

PART II.

THEORY OF SOLID FRICTION.

There have in the past been two main theories of solid friction. According to the first, friction is due simply to a mechanical interlocking of the surface asperities on the solids; according to the second it is due to a molecular attraction between the two solids and should be explicable in terms of surface forces. It is clear, however, from these experiments that the physical processes which occur during sliding are very complex. The friction cannot be regarded as a surface effect. Penetration and distortion occur to a great depth beneath the surface and the frictional force and the nature of sliding are both influenced by the bulk properties of the solids. The physical properties of the solids such as their relative hardness and (if the sliding speed is high) their relative melting point play an important part.

It is suggested that the frictional resistance between unlubricated metals is due primarily to the shearing of the small metallic junctions formed locally at the points of contact and to the work of dragging or ploughing the surface irregularities of the harder metal through the softer one, so that we may write the frictional force F as

$$F = S + P$$

where S is the force required to shear the metallic junctions and P the force required to displace the softer metal from the path of the slider. It follows that $S = As$ where A is the real area of contact of the metals and s the shear strength of the softer metal, while $P = A'p$ where A' is the cross section of the torn track and p is the "flow pressure", i.e. the pressure to cause plastic flow of the softer metal. From this $F = As + A'p$.

When the load is applied to the surfaces, plastic flow of the softer metal occurs at the regions of contact until the area of contact is sufficiently great to support the applied load. With any particular metal, therefore, the real area of contact is determined, primarily, by the load W , and $W = pA$.

$$\mu = \frac{F}{W} = \frac{As}{W} + \frac{A'p}{W} = \frac{\text{shear strength}}{\text{flow pressure}} + \frac{A'p}{W}.$$

If the ploughing term is negligible, it follows that

$$\mu = \frac{\text{shear strength}}{\text{flow pressure}}.$$

By using sliders of appropriate shapes we may evaluate S and P separately and see how far experiment agrees with theory.

A simple case experimentally is that of a cylindrical slider of a hard metal (e.g., steel) resting on a flat surface of a soft one (e.g., lead or indium) (see Fig. 12). The force F required to move the slider forward will be made up of two parts. The first is the force P required to displace the softer metal from the front of the slider and will be equal to the cross sectional area of the grooved track A' multiplied by the flow pressure of the softer metal. The second is the force S required to shear the metallic junctions at the points of adhesion between the two metals.

If the length of the cylinder is zero, i.e., if the slider is in the form of a semi-circular spade (Fig. 12) the work of shearing vanishes and all the frictional work is due to ploughing.

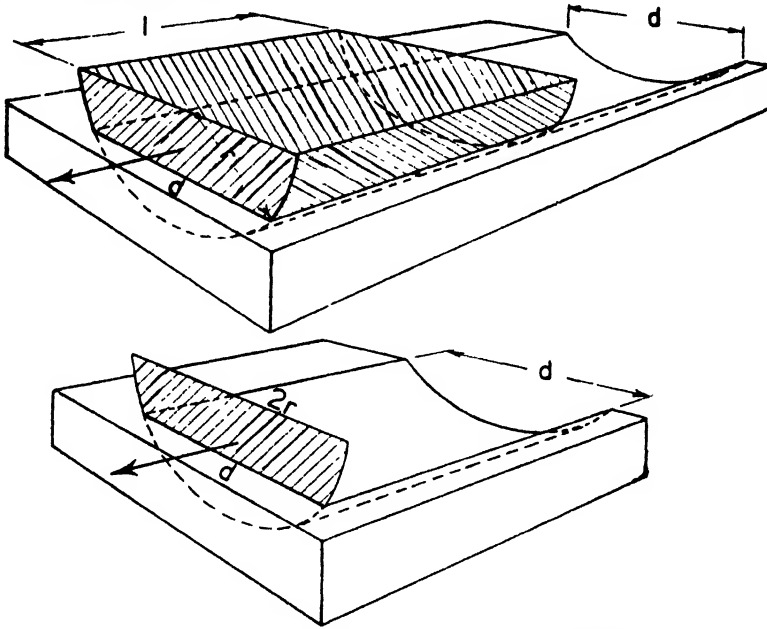


Fig. 12.—(a) A cylindrical cylinder of steel being dragged through indium involves a ploughing force P and a shearing force S . (b) A semi-circular spade being dragged through indium involves only the ploughing force P .

Fig. 13 shows the result of such an experiment with steel cylinders and spades on indium. Curve 1 (F) represents the experimental results for a cylinder,

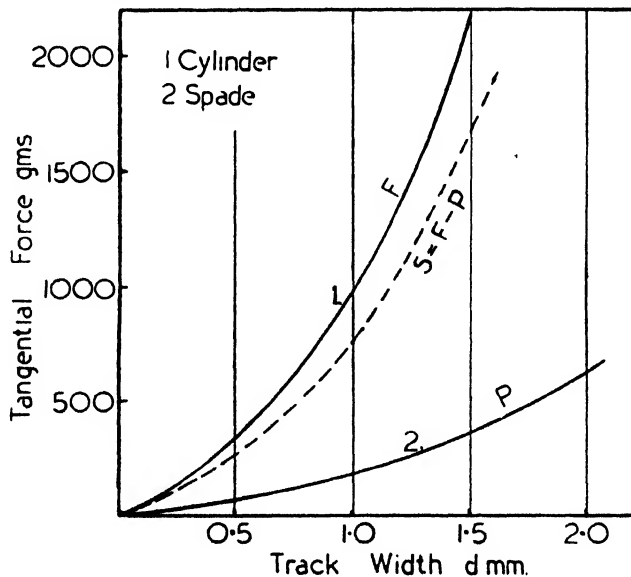


Fig. 13.—Graph showing the frictional force as a function of the track width for a cylindrical slider (Curve 1) and for a spade (Curve 2) sliding on indium. The difference between Curves 1 and 2 gives the shearing term S .

Curve 2 (P) the results for a spade, and Curve 3 the difference between them, gives the shearing term S . It is then possible to compare these experimental values of P and S with the theoretical ones calculated from the flow pressure and the shear strength of indium, and such a comparison shows that the results are in reasonable agreement with the theory, for indium, lead and other metals. It will be noted that the ploughing term P is small compared with the shearing term S .

Elastic and Plastic Deformation. Frictional Hysteresis.

The reality of the welding process is clearly demonstrated when frictional measurements are made with soft plastic metals. With lead or indium, for example, sliding on steel, the value of the friction is very variable and depends on the previous history. If the load is first applied and then decreased or removed altogether, the surfaces continue to "stick" together and the tangential force necessary to cause sliding remains high, although there is no normal load applied between the surfaces. This is not observed on harder, more elastic, metals. For such metals, the frictional force decreases when the load is decreased and the effects are reversible. It is suggested that the elastic deformation of the metals is responsible for this. At the actual region of contact where the local pressures are very high, the deformation of the metals will be plastic. Near this region, however, where the pressures are smaller, the metals will be elastically deformed. When the load is decreased, these stresses will be released and the small movement that results will serve to break the metallic junctions. The area of contact at any given time will, therefore, be determined by the actual load between the surfaces. In the case of a soft plastic metal like indium, however, which shows little elastic recovery, this will not occur, and once the clean surfaces are pressed together they will continue to adhere even when the load is reduced or removed. Similar effects have been observed with gold when its temperature was raised to its softening point. For this reason, measurements of the "coefficient of friction" of an indium slider on a flat steel plate may have little meaning. If, however, the friction is measured as a function of the real area of contact, this difficulty does not arise and consistent results are obtained.

In the experiments described in this paper, the speed of sliding was very low, so that the rise in the surface temperature due to frictional heating was negligible; the melting between the metals is brought about by the intense pressures in the regions of contact. If higher speeds are used, the rise in temperature may be considerable, and a surface softening or local melting may occur. Under these conditions, it is clear that the controlling factor in the frictional behaviour of the metals is not their mechanical properties at room temperature, but their properties at the high temperature of sliding.

The analysis outlined has been applied to metals which differ in hardness. It is clear, however, that the same general considerations apply if the surfaces both consist of the same metal, but since both surfaces are torn, it is not easy to evaluate the ploughing and shearing terms separately. Also the discussion has been confined to metals, but we may expect similar conclusions to hold for many types of non-metallic solids.

Lubrication by Thin Metallic Films.

As we have seen, the frictional resistance between solids may (when P is small) be represented approximately by the expression $F = As$. If then we wish to get a low friction we should make both A and s as small as possible. Unfortunately, with most solids this is not possible. If we choose a solid of low shear strength it usually means that it has a low flow pressure so that when we apply a load to the surfaces the area of contact A becomes correspondingly larger. An obvious exception to this is a solid with a plate-like structure such

as graphite. This is able to withstand a pressure normal to the plates but will shear readily when a tangential force is applied. The friction of graphite is notoriously low. It is difficult to achieve this condition for metals since they are less anisotropic. If we choose a soft metal of low s , A will be large (Fig. 14 (a)). If we choose a hard metal A will be small but s will be great (Fig. 14 (b)). For this reason the friction of most metals is of the same order of magnitude and $\mu \sim 0.6-1.0$.

We may, however, achieve this condition efficiently by depositing a very thin layer of a soft metal on to the surface of a hard one (Fig. 14 (c)). Provided the metallic film does not break down the shear strength will be that of the soft

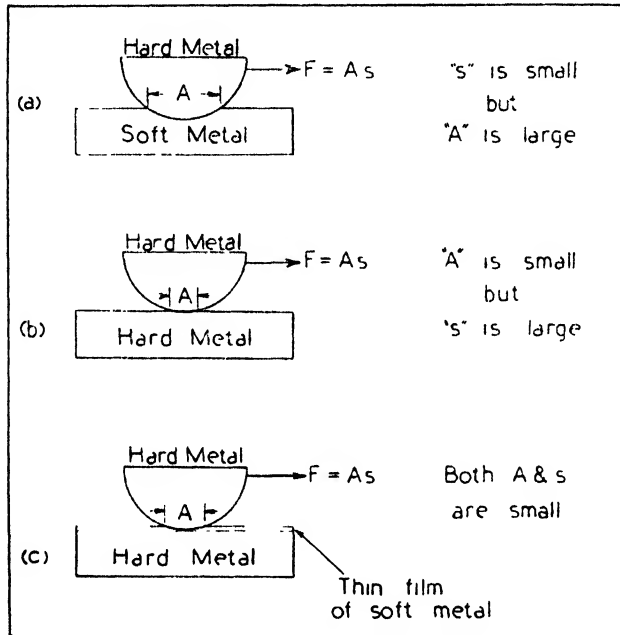


Fig. 14.—The friction between metal surfaces is not greatly dependent on their hardness. A low friction may be obtained by depositing a thin film of a soft metal on a hard metal substrate.

metal. At the same time A will remain small even for heavy loads since it is not greatly affected by the plastic deformation of the hard metals; it is determined essentially by the thickness of the film and the geometry of the surfaces.

A series of experiments was carried out by Dr. Tabor with films of indium, lead and copper of varying thicknesses which were plated on to flat metallic surfaces. The substrate was steel, nickel, copper or silver. The upper surface was a hemispherical steel slider. It was found that the friction is almost independent of the underlying metal and of the load. The main effect of increasing the load is to cause a slight increase in the deformation of the underlying metal, and so cause a slight increase in the track width d . Since silver is softer than steel the same load will produce a greater deformation. The track width d , and hence the frictional force F for any given load and film thickness will, therefore, be greater on silver than on steel. This effect was observed. In Fig. 15, F is plotted against d for lead films deposited on various substrates; the different values of the track width being obtained by varying the thickness of the deposited layer and the radius of curvature of the upper surface. It will be seen that in all cases the frictional resistance is determined, primarily, by the track width, whether the friction is measured on the surface film or on the

bulk metal. Essentially similar results were obtained for indium and copper films. It was also found, as we should expect, that the value of the friction was proportional to the shear strength of the respective metals and for films of similar thickness the friction of copper > lead > indium.

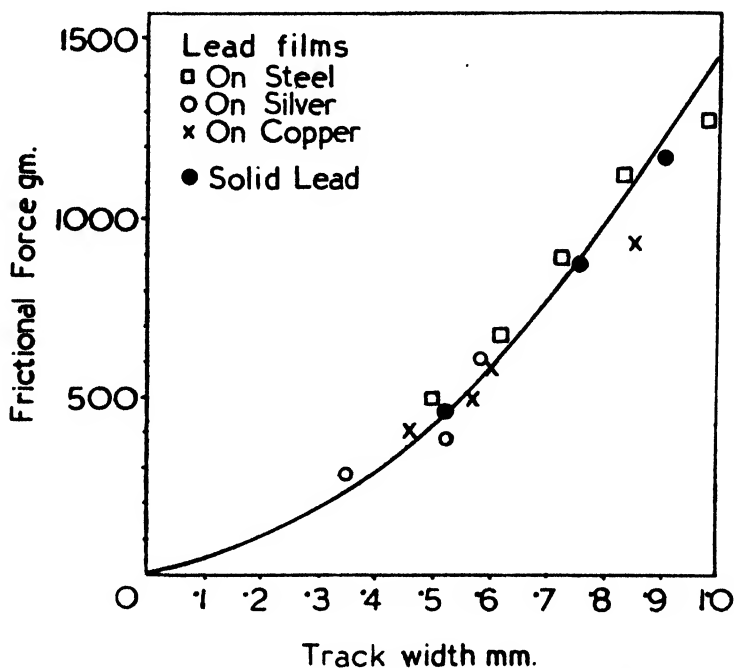


Fig. 15.—Friction of steel slider on lead films deposited on steel, silver and copper substrates, as a function of track width. It is seen that the friction is determined primarily by the track width, whether the friction is determined on the surface film or on the bulk lead.

The Limiting Film Thickness.

Experiments were carried out to determine the minimum thickness of the deposited film that would influence the friction. The results for indium on tool steel are shown in Fig. 16. The film thickness was calculated from the quantity of electricity used to deposit it. The upper curved slider was of hard steel (radius 0.3 cm.) and the load was 4,000 g. As one might expect, the friction decreases as thinner films are used because the area of contact A becomes smaller. There is, however, a limit to this, and a minimum friction is reached when the thickness is of the order of 10^{-5} cm. With thickness less than this, e.g. 10^{-6} cm. (or 50 atomic layers) the film ceases to be effective.

The underlying surface of the tool steel was not highly polished nor was it homogeneous. These factors might easily cause the indium to be deposited preferentially in certain regions, leaving patches of the surface uncovered or only very thinly covered. It is possible that if highly polished surfaces of a uniform metal were used as a substrate, very much thinner layers, even perhaps one or two molecular layers, might prove effective.

Breakdown and Wear of Films.

If very heavy loads are used, the values of F deviate from the curves shown in Fig. 16. After a certain load has been exceeded the friction increases markedly with load, even though the track width remains essentially unaltered. An

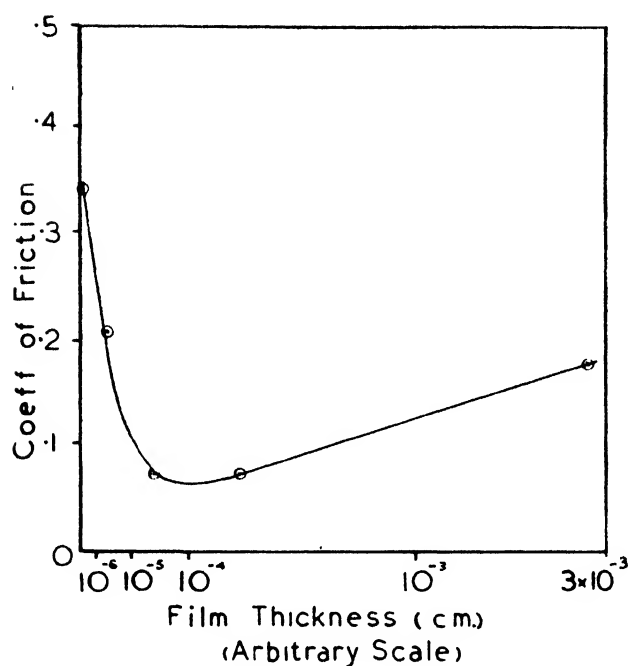


Fig. 16.—The effect of film thickness on the frictional properties of thin films of indium deposited on tool steel. A minimum friction is obtained for a film thickness approximately 10^{-4} to 10^{-5} cm.

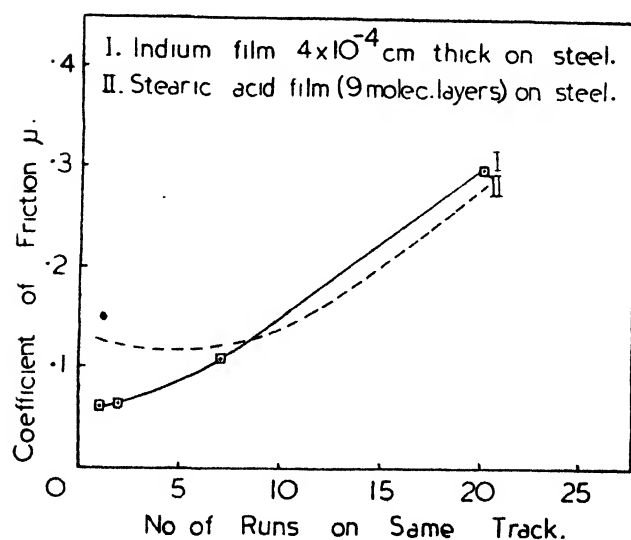


Fig. 17.—Rise in friction with wear of an indium film 4×10^{-4} cm. thick deposited on tool steel. A stearic acid film two hundred times thinner has similar wear resisting properties.

examination of the track shows that this is connected with the progressive breakdown of the film, as the heavier loads are applied. The load at which this breakdown occurs depends upon the film thickness and upon its strength of adhesion to the underlying surface. It is also influenced by the shape of the slider and takes place more readily if this has a small radius of curvature.

The film may also be worn away if the slider traverses the same track a sufficient number of times. With an indium film 4×10^{-4} cm. thick on tool steel the sliding during the first run was smooth and the coefficient of friction was about $\mu = 0.08$. With successive sliding over the same track the friction gradually rose and after the seventh run small "stick slips" set in. The friction and the size of the stick slips increased and after 20 runs μ had risen to about 0.4. Microscopic examination of the surface after the seventh run showed that the indium film had been partially worn away and portions of the steel surface exposed.

The rise in friction with wear of an indium film 4×10^{-4} cm. thick is shown in Fig. 17. With thicker films (not shown in Fig. 17) the rise in friction is less rapid, showing that the thicker film is more resistant to wear. This behaviour may be compared with the dotted curve which represents the rate at which stearic acid layers are worn off a steel surface. We have found that with nine molecular layers of the acid an appreciable rise of the friction occurs after 20 successive runs. With 53 molecular layers, i.e. about 10^{-5} cm., no appreciable change was observed after 100 successive runs. It is clear that the metallic films resist wear quite well, but they are more easily worn off the surface than a much thinner film of the fatty acid. One factor that may be of importance here is the surface mobility of the film. The fatty acid molecules have a certain mobility and are able to move over the surface and repair the damaged film. Many metals also possess this ability to wander over solid surfaces, but it is probable that the rate at which this process occurs is less rapid for solid metallic films than it is for the fatty acids.

Metallic Films as Lubricants.

Some experiments were carried out to determine the extent to which the coefficient of friction μ is independent of the load (Amontons' law). The results for tool-steel surfaces are shown in Fig. 18. Curve I is for the unlubricated steel; Curve II for steel lubricated with a film of mineral oil; and Curve III for steel lubricated with a thin film of indium approximately 4×10^{-4} cm. thick. The comparative behaviour is striking. The coefficient of friction for the unlubricated steel, and for the steel lubricated with the mineral oil, is independent of the load. With the indium film, however, μ decreases markedly as the load increases.

In the case of unlubricated steel, or of steel lubricated with the mineral oil, the area of contact should be proportional to the applied load, since it depends on the amount of plastic deformation that occurs. For this reason F should be directly proportional to the load, i.e., Amontons' law should hold and the coefficient of friction should be constant. This is in fact observed. For the unlubricated steel surfaces, the coefficient of friction is constant and $\mu = 0.34$, while for the surfaces lubricated with the mineral oil, the coefficient of friction is again constant and $\mu = \text{ca. } 0.14$.

If a thin film of a soft metal is used as a lubricant, however, A will no longer be proportional to the load. The real area of metallic contact now increases only to a slight extent when the load is increased, since the increase in A due to the increased deformation of the underlying steel is small compared with its actual value A . The shear strength s remains constant and is approximately that of metallic indium, so that F should be almost independent of the load. Amontons' law will no longer hold, and the coefficient of friction μ will not be constant but will decrease as the load increases. It will be seen from Fig. 18

that this occurs. The coefficient of friction falls from $\mu=0.2$ at the light load to $\mu=0.04$ when the heaviest load is used. If it were possible to lubricate the surfaces with metallic films of molecular dimensions, we should expect a closer agreement with Amontons' law.

In some ways the behaviour of the metallic films closely resembles that of ordinary lubricant films. They produce a substantial reduction in the friction, they can cause smooth sliding, and they protect the underlying metal surfaces. In addition, metallic films are worn off the surface by successive sliding over the same track in a manner similar to that of a lubricant film, except that the metallic films are worn away at a greater rate than the hydrocarbon films. A further point of striking similarity is the effect of melting. The transition from smooth sliding to stick slips when the metallic films are melted, is closely analogous to the change observed when solid hydrocarbon films are heated through their melting point.

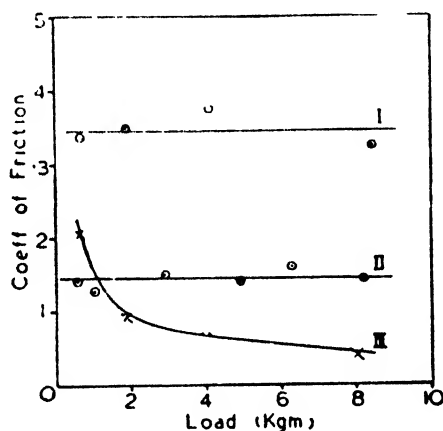


Fig. 18.—Effect of load on the coefficient of friction for unlubricated steel surfaces (Curve I) steel surfaces lubricated with mineral oil (Curve II), and for steel surfaces lubricated with a film of indium 4×10^{-4} cm. thick (Curve III). The coefficient of friction is independent of load for Curves I and II, but rapidly decreases with increasing load for Curve III.

There are, however, several marked differences between metallic films and lubricant films. The earlier experiments showed that even on rough surfaces a lubricant film need only be one molecule thick to be effective as a boundary lubricant (see also Langmuir). A metallic film must be appreciably thicker, of the order of 10^{-5} cm., if it is to be effective. A further striking and fundamental difference is that lubricant films obey Amontons' law and metallic films do not. With metallic films the coefficient of friction decreases as the load is increased, and at high loads the coefficient of friction may be extremely low. With the indium films described in this paper the value of μ under heavy load ($\mu=0.04$) is considerably less than that observed with even the best boundary lubricants. This value is similar to that obtained on ice surfaces.

The Action of Bearing Alloys.

The fact that values of friction as low as this may be obtained with unlubricated metals is of obvious practical interest. For a long time it has been customary to use special metallic alloys which have more desirable frictional

properties than pure metals. The nature and composition of these alloys—bearing alloys they are usually termed—varies widely. The “white metal” alloys are divided roughly into two classes: tin-base alloys, i.e. alloys which consist primarily of tin with various additions such as Sb, Pb, Cu; and lead-base alloys which consist mainly of lead with additions such as Sb and Sn. In general these alloys are complex in structure and contain hard particles dispersed throughout a softer matrix. Another bearing alloy which was developed later and which has found a wide application in aircraft and other engines when the conditions of operation are very severe, is the copper-lead alloy. This is not a true alloy at all but consists of a fine dispersion of lead distributed throughout copper. In one type of the bearing the lead is distributed as minute isolated droplets throughout the copper; in the other, the dendritic type, the lead forms the continuous phase round the copper dendrites.

There is no doubt that the friction of these bearing metals is very much lower than that of the pure metals. Typical values obtained by Dr. Tabor are given in Table 2.

TABLE 2.

Friction of Steel Sliding on Pure Metals and on Bearing Alloys.

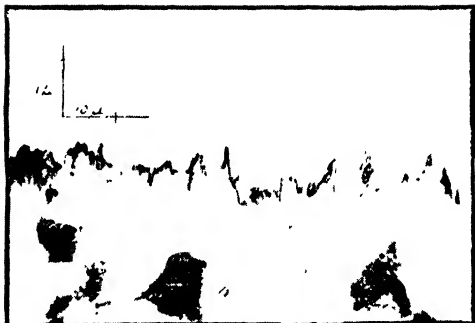
Metal.	Coefficient of Friction.
Tin	0.9
Tin base alloy	0.7
Lead	1.0
Lead base alloy	0.35
Copper	0.9
Copper lead alloy	0.18

The mechanism of this reduction in friction is, however, by no means certain. It has been maintained in the past that an essential characteristic of a bearing alloy is that it should possess a duplex structure consisting of hard crystals embedded in a relatively soft matrix. It is suggested (see, for example, Greaves and Wrighton, 1939) that the function of the hard crystals is to resist wear and that of the softer constituents to permit a more uniform distribution of the load, by allowing any of the hard crystals that are heavily loaded to sink so that the load is spread over a greater area. It is also suggested that the hollows worn in the softer material serve as reservoirs for the lubricating oil. There is probably something in these suggestions, and it is certainly true that many successful bearing alloys do possess a structure of this type. It is clear, however, that it is not a complete explanation and in many cases is certainly not true at all. Many bearing alloys, e.g. copper-lead alloys, may consist of a matrix of the harder metal with a small amount of the softer metal finely dispersed through it.

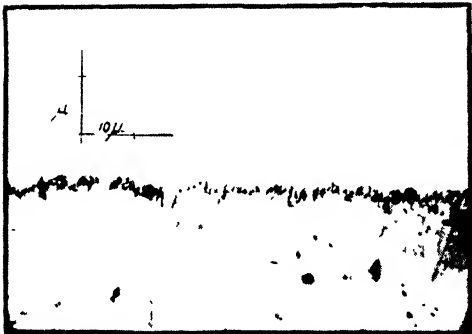
In the case of the non-dendritic copper-lead alloy, for example, the hard copper forms the continuous phase so that it is not possible for it to “sink” into the lead. Why then is the copper-lead alloy so effective in reducing the friction? An obvious suggestion is that it is due to the smearing of a lead film over the surface of the copper. In order to test this a series of experiments was carried out with thin films of lead electrodeposited on to the copper.



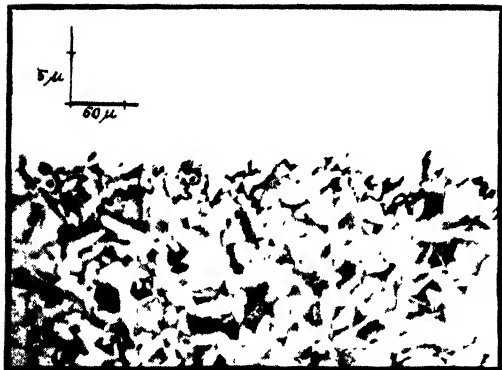
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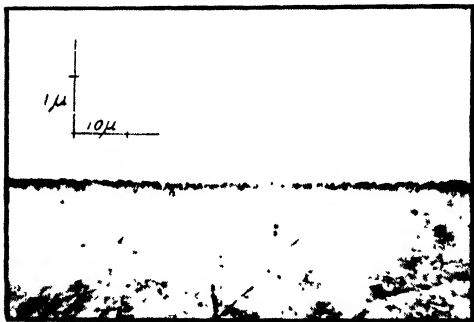
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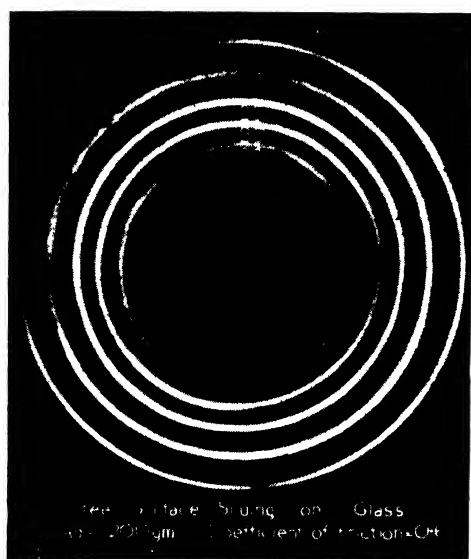
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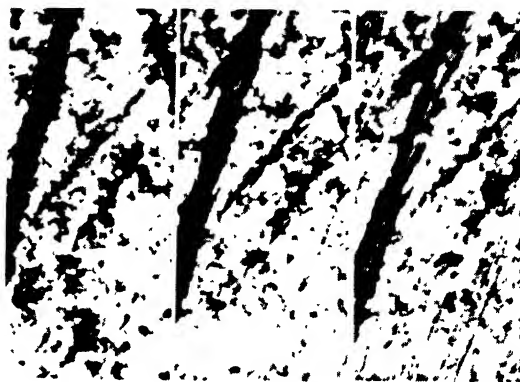
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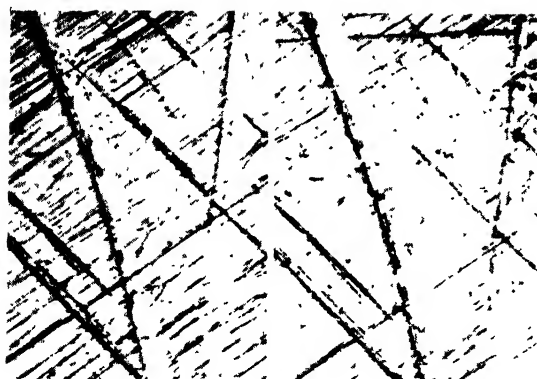


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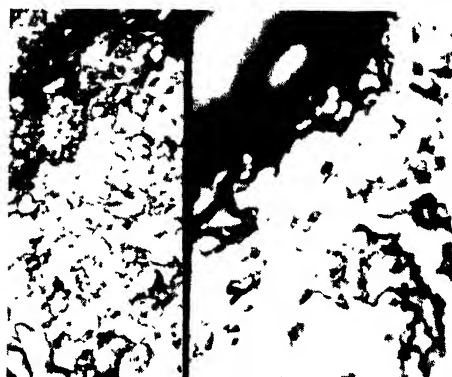
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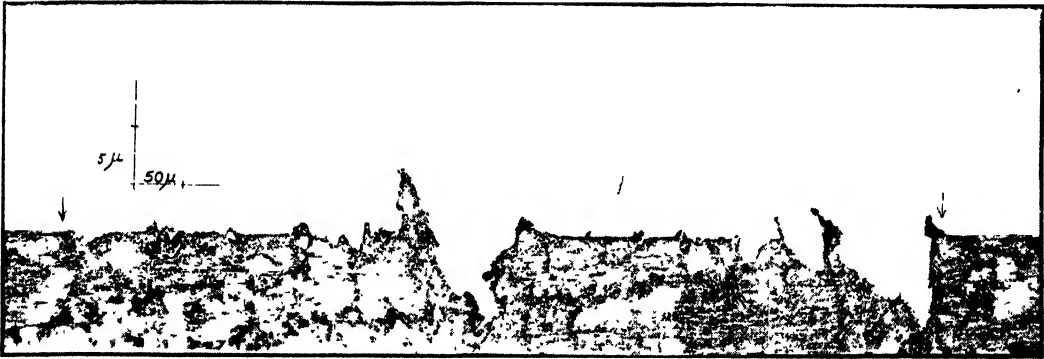


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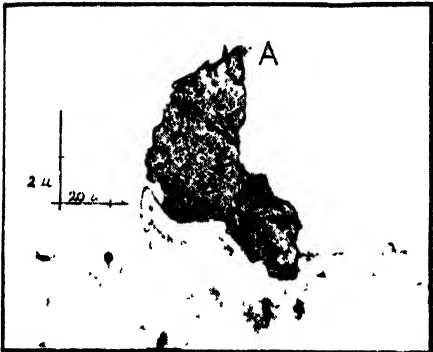
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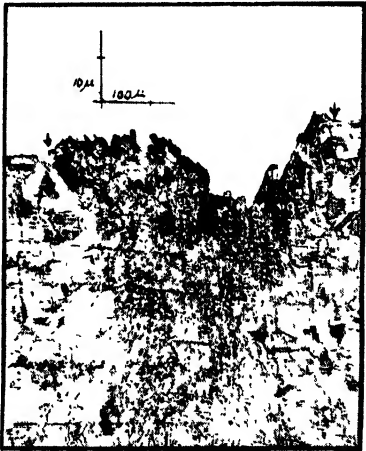
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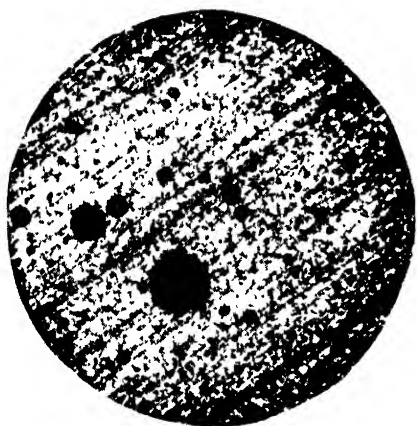
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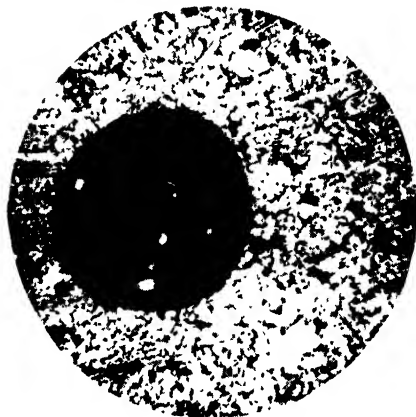
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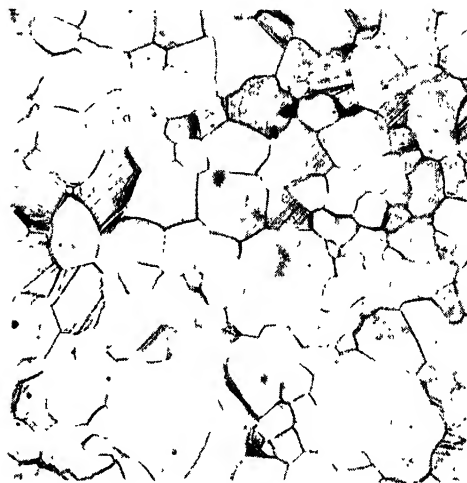
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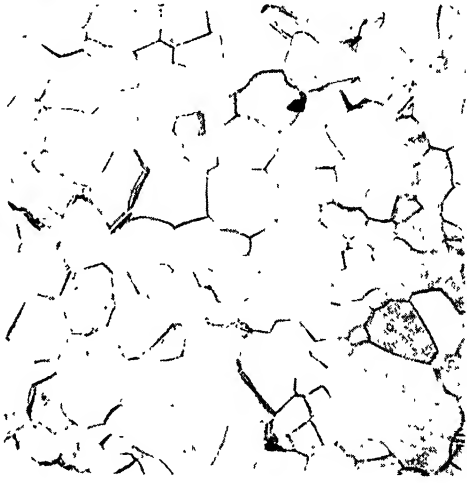
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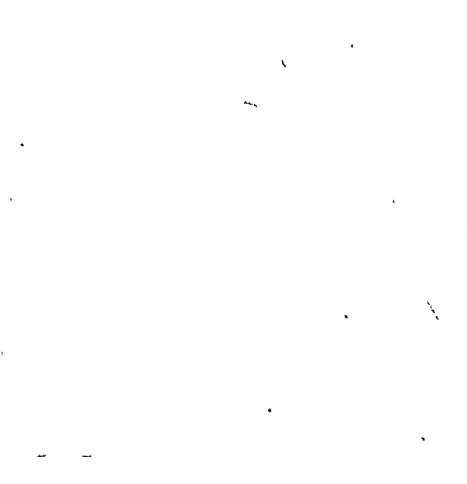
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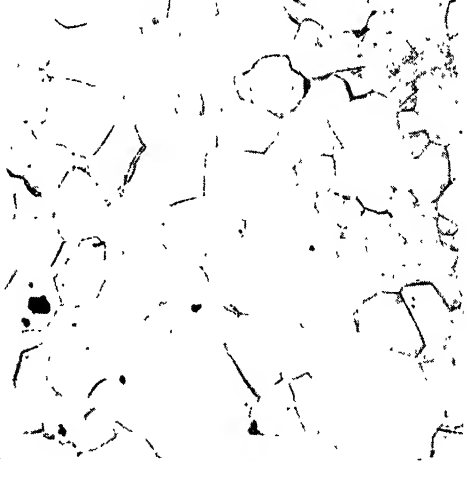
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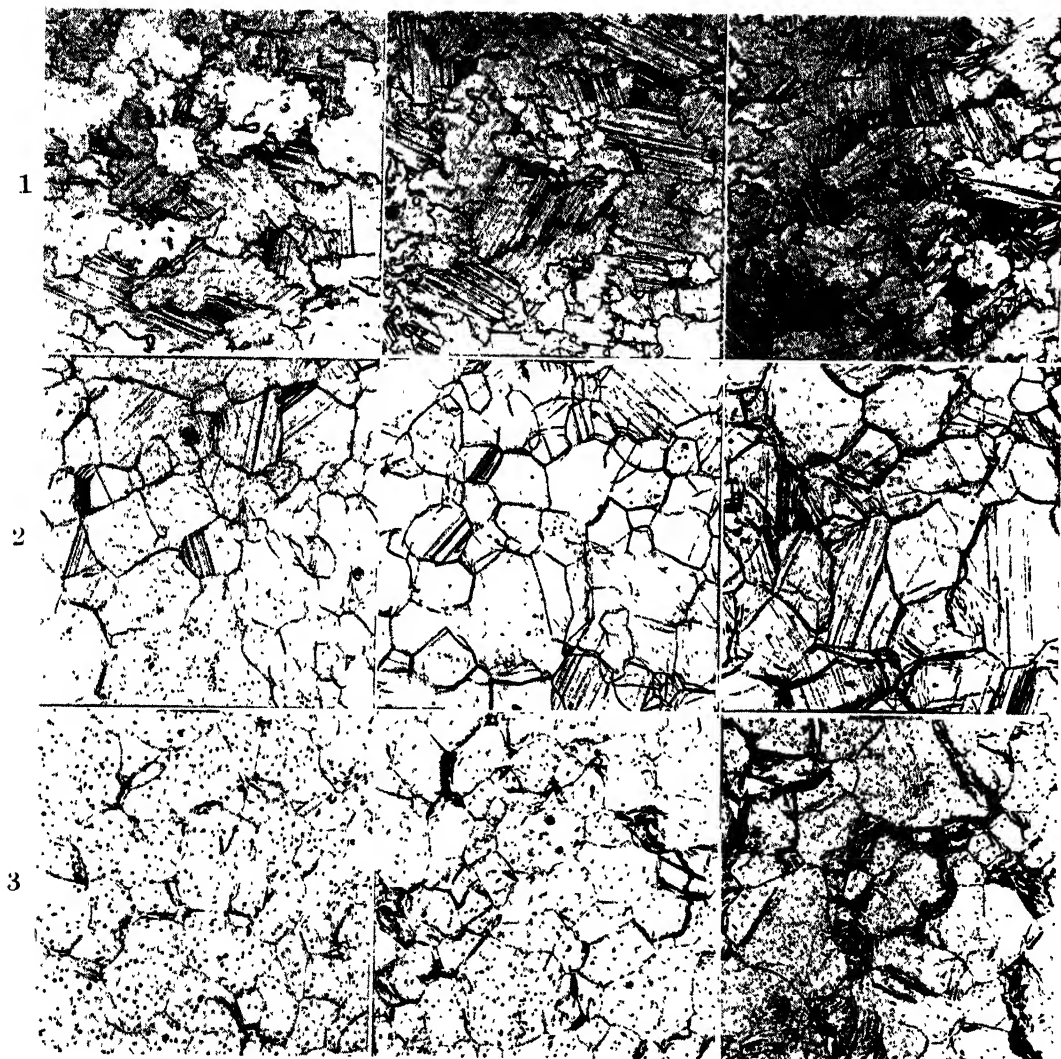
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Thin Films of Lead on Copper.

The relation between the track width and the friction of a curved steel contact sliding on a copper surface which has been coated with lead films of varying thickness is shown in Fig. 19.

A film of lead 10^{-6} cm. thick (Curve II) causes very little reduction in the friction. As the thickness of the film is increased, the friction for any given track width decreases, and reaches a minimum when the film is 10^{-3} cm. thick (Curve V). Further increase in film thickness produces no further change. The frictional force is now governed by the shear strength of the lead and the width of the track and is not influenced by the substrate (except in so far as this

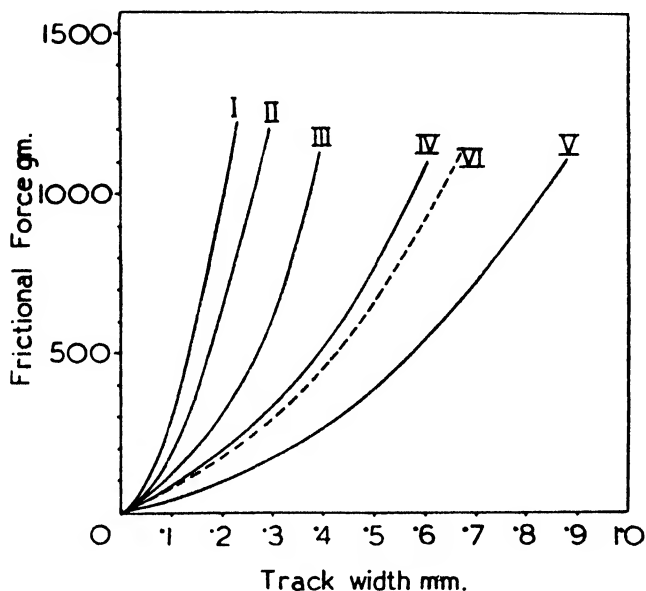


Fig. 19.—Friction of a curved steel contact sliding on a copper surface coated with lead films of varying thickness. I, clean copper; II, lead film 10^{-6} cm. thick; III, lead film 10^{-5} cm. thick; IV, lead film 10^{-4} cm. thick; V, lead film 10^{-3} cm. thick and more and solid lead; VI, lead-copper alloy. The behaviour of the alloy suggests that a thin film of lead is extruded and lubricates the copper matrix.

may affect the track width). When similar measurements are made on solid lead, the points lie on Curve V (Fig. 19). It is clear that after the film has reached a thickness of about 10^{-3} cm. the friction is due to the interaction between the steel and lead. This minimum film thickness of 10^{-3} cm. for lead films on copper is greater than that observed when the films are deposited on steel. It is also greater than that observed when indium films on steel. As pointed out earlier, the minimum film thickness for complete "lubrication" is influenced by the hardness of the metal substrate. With softer metal substrates, such as copper, which are more readily deformed, thicker films are necessary. It is also influenced by the fineness of the original surface finish and by the state of cleanliness of the substrate since this affects the strength of adhesion of the deposited layer.

Copper-lead Alloys.

The frictional behaviour of both dendritic and non-dendritic alloys at room temperature was similar. Steel on the alloys gave smooth sliding and a co-

efficient of friction of about $\mu=0.18$. The tracks were smooth grooves showing little tearing. Some signs of smearing of extruded lead could be detected. The alloys on steel gave stick-slip motion, the maximum value of the friction being about $\mu=0.3$. The tracks showed that some metal from the upper contact had been welded on to the steel surface but the extent of this was considerably less than the welding observed with pure copper or lead.

It is at once apparent that the friction of these alloys does not lie between the values of their constituents. The friction of steel on copper, for example, is about $\mu=0.9$, and for steel on lead $\mu=1.0$. With steel on the copper-lead alloys, however, the friction is about $\mu=0.18$. The alloys and the pure copper have approximately the same flow pressures at room temperature, so that the area of contact A is nearly the same for a given load. Nevertheless the friction of the alloys is less than one-quarter that of their pure constituents.

The relation between the friction F and the track width d for the alloy is plotted on the broken curve (Curve VI) in Fig. 19. It will be seen that these results lie very close to those obtained when a lead film 10^{-4} cm. thick is artificially deposited on to copper. This at once suggests that the lead in the alloys is extruded during sliding and forms a thin "lubricating" film of effective thickness between 10^{-4} cm. and 10^{-3} cm. on the copper. This is borne out by a microscopic examination of the track which showed traces of lead smeared over the surface.

The Role of Thin Films in the Action of Bearing Metals.

We see, therefore, that the frictional behaviour of a copper-lead alloy resembles very closely that of a copper surface on which a very thin film of lead has been deposited. The actual value of the friction of the alloy is the same as that of a copper surface on which a lead film 10^{-4} cm. thick has been artificially deposited. Additional experiments showed that the temperature coefficient of friction was the same in each case. The increase in friction with wear was also very similar except that, in the case of the alloy there is evidence that the potential supply of lead is greater since it may continue to be expressed from the alloy during the sliding process. With a thin film of lead deposited on copper the supply is, of course, limited to the amount which is actually present on the surface at the beginning of sliding.

These results show the important part which may be played by thin surface films of metal in reducing the friction and wear of bearing alloys and support the view that in certain bearing alloys the anti-frictional and anti-seizure properties may be due, primarily, to the spreading of thin films of the soft low melting constituent, over the surface of the harder constituent.

Certain solids are able to provide their own surface films. This is the case, as we have seen, with ice. Under the frictional heating local melting of the surface layers may occur and may provide a lubricating film, while the bulk of the solid remains hard. With most pure metals it is difficult to achieve this, because of the progressive softening of the metal as the temperature is raised which leads to a corresponding increase in the area of contact, so that the friction is little affected. The problem is to keep both the area of contact A and the shear strength s as small as possible.

We see, however, that the condition of small s and small A may be achieved artificially by putting a very thin film of a soft metal on to the surface of a hard one. This may be done by deposition beforehand, or it may be achieved by selecting an alloy of suitable composition and structure so that the film is spread during the sliding process.

In this connection the importance of surface tension is apparent. The soft low melting constituent must spread readily on the harder one to form a thin film. This is borne out by experiment. It was shown, for example, with lead, indium and mercury films on steel, copper and silver that unless the soft metal

readily wetted the harder one, it was, under severe conditions of sliding, relatively ineffective as a lubricant.

Although it is desirable that these metallic films should adhere to and wet the substrate, the converse should be true about the other moving surface, e.g., the journal of a bearing. Provided the metallic film does not break down, the smaller the adhesion and the less the tendency of the metallic film to spread on to this surface the better. As has been pointed out in Part I, one important function of a lubricant is to reduce the adhesion between the two moving surfaces and help to reduce the effective shear strengths of the metallic junctions.

Apart from these surface tension and spreading effects the *availability* of the soft constituent is important. The dendritic copper-lead alloy, for example, may under certain severe conditions of sliding be more resistant to seizure than the non-dendritic alloy. In the former alloy the pockets of lead are all interconnected so that potentially a greater supply of lead is available to any particular area of the surface which may be in need of it. With the non-dendritic alloy the pockets of lead are isolated so that a local exhaustion of the lead may occur and a seizure on to the copper surface may take place. This difference is shown by the "sweating" out of the lead (see Plate XI, Fig. 1). When the non-dendritic alloy is heated, the lead appears as a fine mist of droplets over the surface. When the dendritic alloy is heated the lead collects in one or two large drops, by a surface tension effect (see Plate XI, Fig. 2). The dendritic alloy thus has a three-dimensional supply of lead to the surface while with the non-dendritic alloy it is restricted to the surface layers.

Lubrication by these thin metallic films may be used effectively in a number of practical problems. One of the newer type of bearings which is used in modern aircraft is the silver-lead bearing. The bearing surface consists of pure silver on which is deposited a thin layer of lead or of lead and indium. The silver itself has very desirable mechanical and thermal properties but it gives a high friction and readily seizes on steel. It may, however, be effectively lubricated by a thin film of a soft metal such as lead and indium. It is interesting to note that Atlee, Wilson and Filmer (1940) find that steel ball bearings in a vacuum tube may be effectively lubricated with thin sputtered films of barium and other metals. It is probable that thin metallic film lubrication will find an increasing application in a number of practical operations such as the pressing, drawing and heavy working of metals.

THE EFFECT OF TEMPERATURE CHANGES ON BEARING ALLOYS.

As we have seen, the frictional heat liberated during running may raise the temperature of the surface layer of a bearing to high values, and this may have a marked effect on the mechanical and frictional properties of the bearing. In addition, however, to this localized surface heating the bearing as a whole may be gradually warmed up and cooled down as the engine is started or stopped or as the temperature of the oil changes, and we may enquire what effect these thermal cycles may have on the bearing alloy. If, as is frequently the case, the alloy is bonded on to another metal, we may expect that the difference in the thermal expansion of the two metals may set up thermal stresses near the boundary. In the case of a typical lead-base alloy the coefficient of thermal expansion is $24 \times 10^{-6}/^{\circ}\text{C.}$, while for steel it is ca. $12 \times 10^{-6}/^{\circ}\text{C.}$ If the bearing is heated and cooled through 100°C. or so, the difference in expansion may cause a deformation and cracking of the softer metal. A characteristic example of this is shown in Plate XI, Fig. 3. This effect, which might be expected, is of practical importance, but it is of comparatively small scientific interest. Some recent experiments by Mr. Honeycombe have, however, revealed a new effect. He found that if he heated and cooled a tin-base bearing metal, *unattached* to any steel, through a temperature range of ca. 100°C. , deformation and cracking

occurred throughout the mass of the metal (see Plate XI, Fig. 4). A lead base alloy treated in the same way showed no such effect. The rate of heating and cooling did not affect the phenomena. In some cases the heating and cooling for a single thermal cycle took as long as seven hours. This shows that the effect is not due to a thermal gradient in the specimen, i.e., it is not due to a heating of the outside (with consequent thermal expansion) while the inside is cool.

To what, then, is it due, and why does it occur with tin-base and not with lead-base alloys? A study of the behaviour of pure metals carried out jointly by Dr. Boas and Mr. Honeycombe (1944) has given the explanation. It is found that pure lead shows no deformation. On the other hand pure tin shows plastic deformation as indicated by distortion at the grain boundaries (see Plate XI, Fig. 5). In cadmium and zinc the deformation is still more pronounced, and slip lines can be detected in these metals when they are heated through only one cycle between 30° C. and 150° C. Migration of the grain boundaries is also observed. The progressive deformation of cadmium with successive cycles is shown in Plate XII, Figs. 1-6 and the deformation is shown even more clearly in Plate XI, Fig. 6. The effect of a larger number of cycles on zinc, cadmium and tin is shown in Plate XIII, Figs. 1-3. As the number of cycles is increased signs of plastic deformation appear in more grains and become more pronounced in individual grains until finally most grains are affected.

Now pure lead is a cubic metal. It is isotropic and its coefficient of thermal expansion α is the same along all the crystal axes. These other metals are non-cubic and their expansion along the different crystal axes is different. With tin, for example, α parallel to the crystal axis, is twice as great as α at right angles to the axis. In the case of zinc it is about four times as great. It is this anisotropy of thermal expansion along the different crystal axes which is responsible for the deformation. In the polycrystalline metal, if we consider any two crystal grains in contact, the chances are that their orientation will not be similar so that when the metal is heated, the expansion on two sides of the grain boundary is different. This necessarily results in plastic deformation and slip in the crystals. This behaviour is therefore a fundamental property of polycrystalline metals themselves. It means that it is very difficult to prepare any anisotropic metal, or in fact any anisotropic crystalline solid, in a state free from strain, since the preparation usually involves some heating or cooling. Even if it is initially free from strain, these strains are readily set up by small changes in temperature. The results are therefore of some theoretical interest from the point of view of the theory of the strength of materials and the physical properties of metals. The work is still in the early stages and it is not yet possible to say of what importance it is practically. It may be a contributing cause to the deformation, cracking, and failure of bearing and other alloys which are observed in service.

THE INFLUENCE OF SURFACE FILMS.

The Addition of Films.

We have seen that the effect of sliding one surface over another is really a pretty far-reaching and disastrous one. Although to the naked eye, or even to the high-power microscope, there may appear to be little change, yet on a molecular scale an enormous tearing, welding and deformation has occurred. If the sliding is continued this ultimately becomes manifest as a wear or perhaps as a seizure of the surfaces. From time immemorial it has been customary to add various films, lubricants or greases to the surfaces in an attempt to prevent or to mitigate this damage. The first really systematic investigation of thin film lubrication or boundary lubrication was made by Sir William Hardy (1936), who measured the static friction between surfaces using homologous series of

long chain paraffins, fatty acids and alcohols as the lubricants. In a series of simple and beautiful experiments he showed that the coefficient of *static* friction decreased linearly with the increasing chain length of each family of compounds. The friction also depended on the nature of the underlying solid surface. He was thus able to show that the friction was a function of separate contributions by the solid surface, the chemical series to which the lubricant belonged, and the number of carbon atoms in the chain. Hardy explained these results by a very simple and elegant theory. He assumed that the friction between unlubricated solids is due to the surface fields of force. When the lubricant is added the lubricant molecules orient themselves at each of the solid surfaces to form a unimolecular adsorbed film. The solids sink through the lubricant layer until they are separated by only the unimolecular adsorbed film of lubricant on each surface. Slip then takes place between these two adsorbed films; the friction is due to the interaction between the outside surfaces of the two adsorbed mono layers (see Fig. 20(a)).

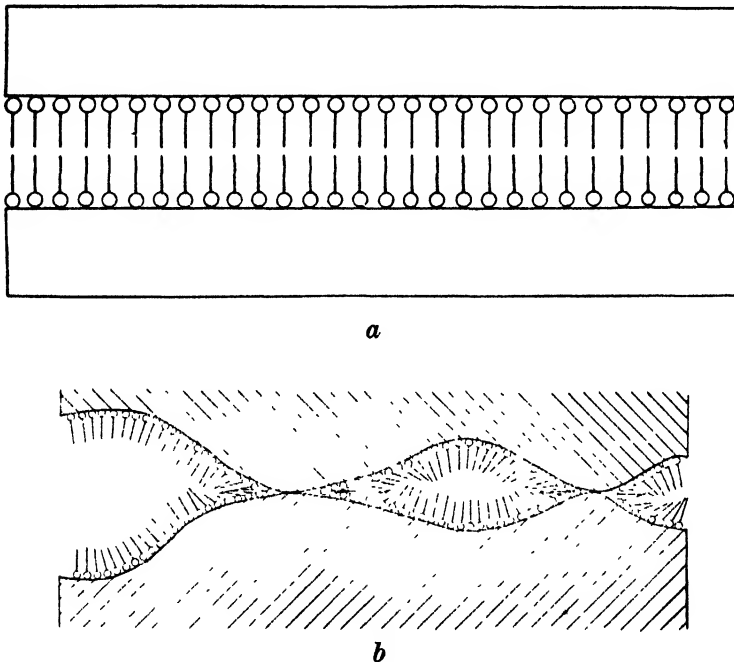


Fig. 20.—The sliding of solid surfaces under conditions of boundary lubrication.

- (a) Hardy's view which envisages interaction between the outer surfaces of the adsorbed monolayers, without any metallic contact occurring.
- (b) Mechanism involving a breakdown of the lubricant film at small localized regions. The metallic junctions so formed are mainly responsible for the friction and wear observed.

As pointed out earlier, however, the interaction between moving solids is not confined to the surface; also we find that a layer even of the best lubricant is not able to prevent the occurrence of contact between the surfaces. Small localized breakdowns of the film occur (see Fig. 20 (b) and when sliding takes place the surfaces are damaged to a great depth.

Unfortunately there is not space in this lecture to deal with the interesting subject of lubrication. Before finishing, however, I would like to mention one more point, that is, the effect of removing the surface films which under normal conditions are always present even on the cleanest surfaces.

The Removal of Surface Films.

Experiments on electron diffraction and electron emission as well as optical and other methods have made it abundantly clear that when a solid is cleaned in air by any ordinary method its surface is still covered by a film of oxide, water vapour, and other adsorbed impurities. The surface film is often many molecular layers in thickness. Any complete theory of friction must take this film into consideration. Most experiments on the friction of metals are not made with metallic surfaces at all but with a metal coated with this surface film. If a lubricant is used, it is not added to the metal directly, but is superimposed on a film of the contaminant.

It is difficult to remove the last adsorbed film and to maintain the surfaces clean. With metals, for example, this can only be done by heating to a high temperature in a very low vacuum. Dr. Hughes (1939) has carried out experiments of this type with a metal cylinder sliding on a wire. The experiments were carried out in a vacuum of ca. 10^{-6} mm. of Hg and both the cylinder and the wire were cleaned and degassed by heating to 1000°C . The effect of removing this adsorbed film of oxygen and other contaminants from nickel and tungsten surfaces is shown in Fig. 21 (a). When the surfaces are really clean the friction rises from its normal value of $\mu = \text{ca. } 0.3$ to $\mu = \text{ca. } 6$. Similar results for copper are given in Fig. 21 (c).

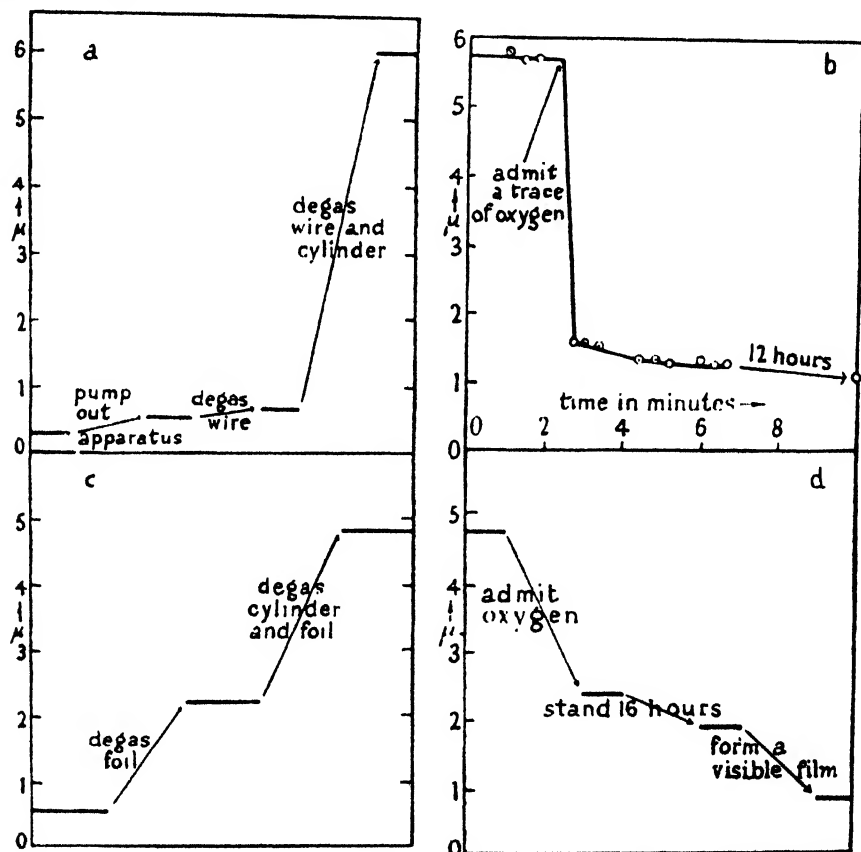


Fig. 21.

- (a) and (c) Effect of removing the adsorbed film of oxygen and other contaminants from metal surfaces, (a) nickel on tungsten, (c) copper on copper. The friction rises by a factor of nearly twenty.
- (b) and (d) Effect of deliberately adding a trace of oxygen, (b) nickel on tungsten, (d) copper on copper. There is a rapid reduction in the friction.

If the clean surfaces are allowed to stand at room temperature in a vacuum of 10^{-5} to 10^{-6} mm., a steady decrease in friction occurred. This decrease occurred in a few minutes and is due to the gradual contamination of the surfaces by residual gases in the apparatus. If we can get rapid contamination under these conditions it is clearly impossible under ordinary experimental conditions to get surfaces which, from the frictional point of view, are really clean.

The effect of deliberately adding a trace of oxygen is shown in Fig. 21. It is seen that there is a rapid reduction in the friction. On the other hand, adding pure hydrogen or pure nitrogen had no effect in reducing the friction of clean surfaces.

The observation that the friction of naked metals is very high (some 20 times greater than that of the normally clean metals) makes us realize how fortunate it is that, in engineering practice and, in fact, in many everyday affairs, metal and other surfaces are contaminated with oxides and other films. If it were not for the fact that metal surfaces (even when we think that we have cleaned them thoroughly) are coated with comparatively thick layers of oxide, "dirt" and other contaminants, much of our machinery would come to a sudden and disastrous stop.

ACKNOWLEDGMENT.

I would like to express my thanks to the Royal Society of New South Wales for inviting me to give these lectures and for its generous and genial hospitality during my stay. I am glad to have this opportunity of acknowledging my indebtedness to the Executive of the Council for Scientific and Industrial Research, with which I have been associated (although necessarily in a temporary capacity) for the past few years. There is no doubt that the stimulating atmosphere within this organization, the encouragement that is given to fundamental work, and the facilities provided for it, are such as to attract to Australia scientific workers of the first rank. I would also like to thank the University of Melbourne for its active collaboration, and in particular Professor E. J. Hartung, who has provided us with laboratory accommodation and with wise guidance.

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EXPLANATION OF PLATES.

PLATE VIII.

Taper Sections of Metal Surfaces prepared in various ways.

(Note: $1\mu=10^{-4}$ cm.)

Fig. 1.—Pin scratch made by fine steel pin on copper surface. Horizontal magnification $\times 130$; vertical magnification $\times 1300$. Note the built-up edges and also the work hardening of the metal which extends to a considerable depth below the original surface.

Fig. 2.—Finely machined steel surface. Horizontal magnification $\times 130$; vertical magnification $\times 1300$. The surface irregularities are of the order of $1\text{--}2\mu$.

Fig. 3.—Steel surface lapped with 150 wet carborundum paper. Horizontal magnification $\times 650$; vertical magnification $\times 6,500$. The surface irregularities are of the order of $0\cdot 3\text{--}1\mu$.

Fig. 4.—Steel surface lapped with 320 wet carborundum paper. Horizontal magnification $\times 650$; vertical magnification $\times 6,500$. The surface irregularities are of the order of $0\cdot 2\text{--}0\cdot 4\mu$.

Fig. 5.—Steel surface lapped with 600 wet carborundum paper. Horizontal magnification $\times 650$; vertical magnification $\times 6,500$. The surface irregularities are of the order of $0\cdot 1\mu$.

PLATE IX.

Fig. 1.—Photographic record of hot spot produced by a steel pin running on a glass plate (load 1,200 gm., coefficient of friction 0.6).

Fig. 2.—Result of rubbing Wood's metal (M.P. 69°C.) on a camphor polisher (M.P. 178°C.) $\times 145$. (a) Start (b) After 1 hour (c) After two hours of polishing. Surface flow has occurred.

Fig. 3.—Result of rubbing speculum metal (M.P. 745°C.) on an oxamide polisher (M.P. 417°C.) $\times 153$. (a) Start (b) After half hour of polishing. No surface flow has occurred.

Fig. 4.—Effect of rubbing calcite (M.P. 1333°C.) (a) on cuprous oxide polisher (M.P. 1235°C.), after half an hour there is no sign of surface flow; (b) on zinc oxide polisher (M.P. 1800°C.), after five minutes there is marked surface flow.

Fig. 5.—Tracks formed (i) when steel slides on copper; the steel has ploughed out and torn the copper surface. (ii) When copper slides on steel; the steel is scarcely damaged but fragments of copper remain adhering to the steel surface. (iii) When nickel slides on nickel; the damage to the surface is very heavy.

PLATE X.

(Note: $1\mu=10^{-4}$ cm.)

Fig. 1.—Characteristic taper-section of steel sliding on steel. Horizontal magnification $\times 120$; vertical magnification $\times 1200$. A considerable portion of the surface is undamaged but a number of regions show marked penetration, ploughing and tearing of the surface. The depth of the torn channels is $1\text{--}10\mu$.

Fig. 2.—Taper-section of copper sliding on steel. Horizontal magnification $\times 120$; vertical magnification $\times 1200$. Fragments of copper *A* are left welded on the hard steel surface *B*, whilst the steel itself is scarcely damaged except at the hollows and pits *C*, where the copper has plucked out fragments of steel.

Fig. 3.—Higher magnification of a copper fragment *A* welded on to a steel surface. Horizontal magnification $\times 300$; vertical magnification $\times 3000$. Note the portion of steel which has been dragged above the original surface level. This illustrates one mechanism by which a soft metal may cause wear of a harder metal.

Fig. 4.—Taper-section of copper sliding on copper. Horizontal magnification $\times 60$; vertical magnification $\times 600$. There is marked ploughing and tearing and the deformation and work hardening of the metal extend to a considerable depth below the surface.

PLATE XI.

Fig. 1.—The "sweating" out of the lead from non-dendritic copper-lead alloy.

Fig. 2.—Dendritic copper-lead alloy after heating above 330°C. ($\times 36$.) With the dendritic alloy the lead collects into a single drop on account of surface tension effects. With the non-dendritic alloy the lead globules remain unconnected.

Fig. 3.—Cracking at the bond between a lead-base bearing alloy and steel. ($\times 165$.)

Fig. 4.—Area of a tin-base bearing alloy after 50 cycles between 30°C. and 150°C. ($\times 33$.) The alloy was not attached to a steel shell.

Fig. 5.—Tin, showing distortion at a grain boundary after 50 cycles between 30°C. and 150°C. ($\times 330$.)

Fig. 6.—Cadmium showing deformation produced after 10 slow cycles between 30°C. and 150°C. ($\times 65$.)

PLATE XII.

An area on a cadmium specimen after various numbers of thermal cycles between 30° C. and 150° C. ($\times 63$.)

Fig. 1.—As polished. Fig. 2.—1 cycle. Fig. 3.—3 cycles. Fig. 4.—5 cycles.

Fig. 5.—10 cycles. Fig. 6.—15 cycles.

The progressive deformation is very clearly marked.

PLATE XIII.

Deformation produced after 50, 100 and 200 cycles between 30° C. and 150° C. ($\times 70$.)

Fig. 1.—Zinc. Fig. 2.—Cadmium. Fig. 3.—Tin.

The deformation after 200 cycles is extremely marked for all three metals.

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PART IV

THERMAL CONDUCTIVITY FROM MEASUREMENTS OF CONVECTION.

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(1) INTRODUCTION.

The measurement of the thermal conductivity of a liquid has always been a problem of peculiar experimental difficulty, this mainly on account of the elaborate precautions necessary to avoid swamping the small heat losses due to true molecular diffusion by the much larger losses due to convection currents. We accordingly find that there are very few reliable figures for the thermal conductivities of liquids and still fewer for the temperature coefficient of the thermal conductivity. From the point of view of the designer of chemical engineering equipment this constitutes an unfortunate omission from the tables of available physico-chemical properties, for the property of thermal conductivity and its temperature coefficient enters into all problems of the design (to a stated capacity) of all equipment for handling fluids undergoing temperature changes, such as condensers, evaporators, reaction vessels, heating and cooling coils and heat exchangers. In the absence of suitable data for the thermal conductivity of all but a few of the best known liquids it is necessary to allow far wider "factors of safety" that would otherwise be required.

While the property of thermal conductivity enters into the dynamics of heat exchangers of all types, in none are we concerned solely with true molecular diffusion. In all cases heat is carried by forced or natural convection, or both, and the thermal conductivity enters the problem solely as one of the physical variables in the dimensionless parameters used for the correlation of data on these more complicated modes of heat transfer. It would seem reasonable therefore to attempt to obtain figures for the thermal conductivities of liquids by reversing this process, i.e. by measuring convective heat losses under standardized conditions and computing from these measurements the thermal conductivity by arguments based on dimensional analysis. While such a method may not have the rigorous theoretical foundation of a proper detailed analysis, nevertheless it uses an approach which is precisely the same as that which is later to be made in the application of the measured figures to design purposes and for this reason has both the numerical and nominative accuracy required for the purposes for which it is to be used.

Perhaps the best known example of convective heat loss is that of the natural convection from a heated horizontal cylinder in a fluid, and we will now proceed to consider methods whereby the thermal conductivity of a fluid can be estimated from measurement of convection from a cylinder in it.

(2) THEORY.

If we have a long horizontal cylinder of diameter d , in a fluid of conductivity k , of viscosity η , density ρ , of thermal (volumetric) coefficient of expansion β and of specific heat c , if θ is the excess temperature of the cylinder surface above that of the liquid and g is the acceleration due to gravity; then it can be shown

by dimensional analysis that the heat loss factor h , measured in units of heat loss per unit area per unit time per unit temperature difference, is given by

$$h = \frac{k}{d} F \left(\frac{d^3 \rho^2 g \beta \theta}{\eta^2}, \frac{c \eta}{k} \right) \dots\dots\dots (1)$$

Apart from showing that the function F is universal, dimensional analysis does not give any indication as to its value. The two variables which determine F are known as the Grashof and the Prandtl numbers respectively. Experimentally F appears to be a function only of the product of the Grashof and the Prandtl numbers. Thus we write

$$h = \frac{k}{d} F \left(\frac{d^3 \rho^2 c g \beta \theta}{\eta k} \right) \dots\dots\dots (2)$$

Equation (2) appears to apply to all fluid systems except liquid metals (for which the Prandtl number is extremely small). The function F has been determined empirically from the ensemble of recorded observations of the convective heat loss from heated cylinders. Most authors have attempted to correlate their observations in terms of power functions. For brevity we shall write the dimensionless quantity $\frac{hd}{k}$, or the Nusselt number as Nu ; and $\frac{d^3 \rho^2 c g \beta \theta}{\eta k}$, or the product of the Grashof and the Prandtl numbers as Gp . Lander (1942) has stated that the observations of earlier writers can be represented by the equations

$$\text{For } Gp \text{ from } 10^3 \text{ to } 10^7 \text{ by } Nu = 0.49 (Gp)^{0.25} \dots\dots\dots (3)$$

$$\text{For } Gp \text{ from } 10^7 \text{ to the limit of observations by } Nu = 0.12 (Gp)^{0.33} \dots\dots\dots (4)$$

For lower values of Gp the variation of Nu with Gp becomes progressively less and less than the fourth root, and for Gp less than 10^{-5} Nu is practically a constant. The empirical function showing the variation between $\log Nu$ and $\log Gp$ is reproduced as Figure 1. It will be appreciated that at very low values of Gp Nu becomes a constant. It would seem desirable therefore to seek an empirical equation for F in the form

$$Nu = A + B Gp^n \dots\dots\dots (5)$$

in which we have split the total heat loss factor into two parts; the one $B Gp^n$ representing the heat carried away by convection currents and the other A the heat carried away by a molecular conduction or diffusion across the filaments of the convection current. While an equation of the form (5) can be made to give better correlation of the existing data than any single power function nevertheless much better correlation still can be obtained by the equation

$$\sqrt{Nu} = \sqrt{A} + \sqrt{B} (Gp)^n \dots\dots\dots (6)$$

Figure 2 shows the "recommended points" from Figure 1 plotted as $\log (\sqrt{Nu} - 0.63)$ against $\log Gp$. The points are linear within the limits of experimental accuracy over the range of Gp from 10^{-5} to 10^9 . Inserting the values of the constants in equation (6) it becomes

$$\sqrt{Nu} = 0.63 + 0.35 Gp^{1/4} \dots\dots\dots (6a)$$

$$\text{or } Nu = 0.40 + 0.44 Gp^{1/4} + 0.12 Gp^{1/2} \dots\dots\dots (7)$$

Just what significance, if any, can be attached to this equation is not entirely clear, but at the moment we are concerned solely with the fact that it

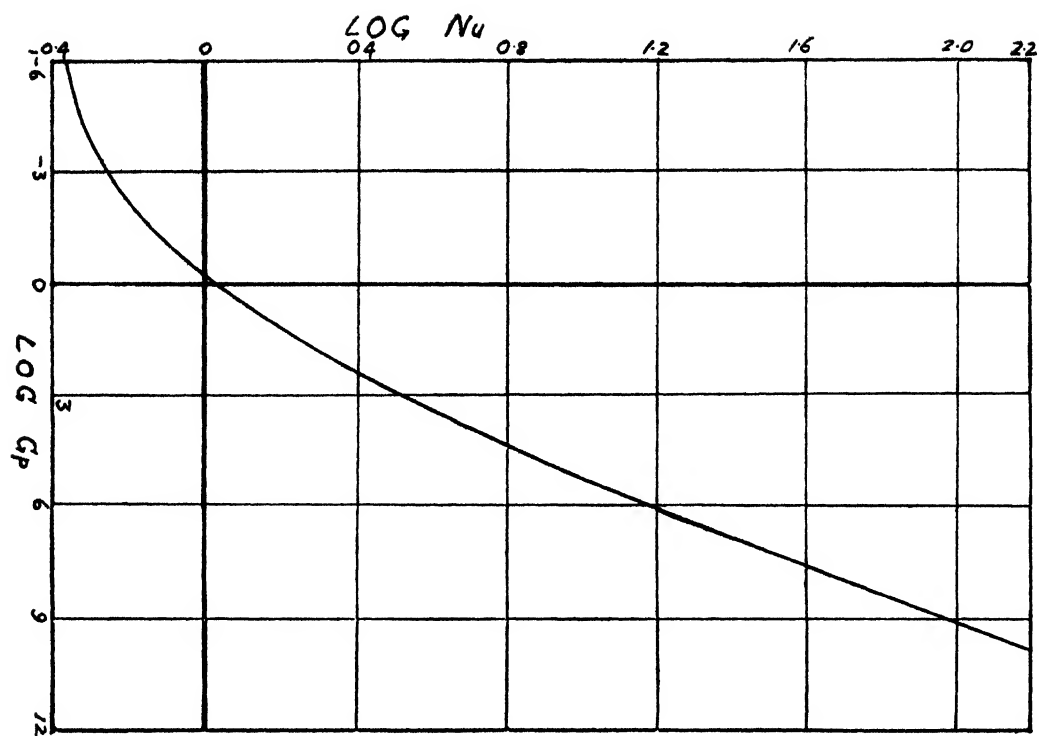


Fig. 1.

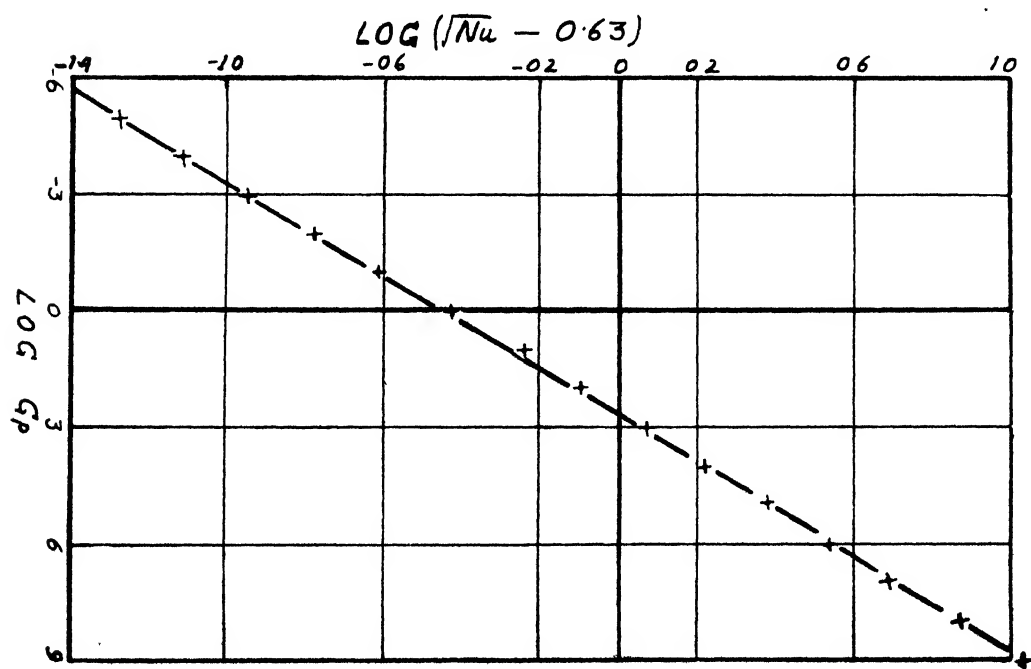


Fig. 2.

does fit experimental data extremely well and this equation provides a simple method of calculating k from measurements of h at different values of θ . Suppose, for example, we have a heated cylinder (or wire) in a liquid. We measure h at a number of values of θ and plot

$$\sqrt{h} \text{ versus } \theta^{1/2}.$$

the points will lie on a straight line which if extrapolated to cut the axis of h at, say h_0 , will give

$$\sqrt{\frac{h_0 d}{k}} = 0.63 \dots\dots\dots (8)$$

$$\text{or } k = 2.5 d h_0 \dots\dots\dots (9)$$

so that by measuring the diameter of the wire and the limiting value of h as θ tends to 0, we can obtain the required factor k , the thermal conductivity of the liquid.

(3) PRACTICAL CONSIDERATIONS.

The method proposed consists in setting up a wire heated by an electric current and measuring the heat (q) dissipated per unit time per unit area (or the electrical power consumed per unit area of wire) and the excess temperature θ . $\sqrt{q/\theta}$ is then plotted against $\theta^{1/2}$ and the line is extrapolated to zero θ . If the extrapolation is to be accurate the slope of the resultant line multiplied by any abscissa in the working range must not be too large in comparison with the intercept. In other words investigation should be restricted to the tail of the curve shown in Figure 1. The diameter of the wire should therefore be selected so that, at the maximum working temperature the value of Gp should not exceed unity, or

$$\frac{d^3 \rho^2 c g \beta \theta}{\eta k} \leq 1$$

for all working values of θ . The expression for Gp is commonly written in the form

$$a d^3 \theta$$

where d and θ depend on the wire concerned and a is a specific property of the liquid and is known as the convection modulus. In C.G.S. units a for water at 20° C. is 14,000 and for ethyl alcohol at the same temperature a is 77,000. Most other limpid organic liquids have values of a of the same order as that for alcohol. For very viscous liquids such as glycerine or concentrated sugar solutions a may be much smaller. We will assume that a value of 100,000 for a will cover the most unfavourable case likely to be encountered. Then if $a d^3 \theta$ is to be less than unity for, say, $\theta = 10^\circ \text{C.}$, we must have d not greater than 0.01 cm. or 0.1 mm.

For more viscous liquids higher values of d are allowable. For water at 20° C. and with the other restrictions as postulated d could be up to 0.2 mm. The wires required for this method of measuring thermal conductivity although fine are not excessively so.

A measurement of q will always give the total heat loss from the wire. Now there are three modes whereby the wire may lose heat to the liquid :

- (a) by thermal radiation ;
- (b) by conduction and convection in the liquid ; and
- (c) by conduction along the leads.

For fine wires, such as required by the condition considered above, radiation is negligible in comparison with convection except in the higher ranges of temperature. Factor (c) on the other hand cannot be dismissed so lightly. As

the result of lead conduction the ends of the wires are cooler than the centres and the effective length of the cooled ends is the longer the larger the metallic thermal conductivity in comparison with h , the heat loss in the liquid, and consequently the length of cooled ends will change as the temperature of the wire is changed, so that the rate of heat loss is changed. If q is the rate of development of heat per unit volume of the wire and k' the thermal conductivity of the material of the wire, then provided the heat flow from the surface is constant over the length of the wire, it may readily be shown that the temperature excess θ at a distance x from the lead is given by

$$\theta = \frac{q}{2k'\alpha^2}(e^{-\alpha x} - 1) \dots\dots\dots (10)$$

where α^2 has been written for $\frac{2h}{rk'}$, r the radius of the wire and h the heat transfer factor from the surface.

The fraction of the total heat lost by lead conduction is therefore reduced to 5% when

$$\alpha x = 3 \\ \text{or } x = \sqrt[3]{\frac{rk'}{2h}} \dots\dots\dots (11)$$

Since we are concerned with the limiting case of convection at very low values of Gp , we can write for h

$$h = 0.4 \frac{k}{d} = 0.2 \frac{k}{r}$$

where now k is the thermal conductivity of the liquid. Condition (11) now becomes

$$x = 2.4d \sqrt{\frac{k'}{k}} \dots\dots\dots (11a)$$

as the length of the wire which reduces to lead loss to 5% of the total heat loss. For a typical organic liquid, ethyl alcohol k is 0.10 B.Th.U./hr./ft.²/° F. per foot.

For a typical metal alloy, Constantan, k' is 13 in the same units. $\sqrt{\frac{k'}{k}}$ for such a combination is 11.4, and we have

$$x = 28d.$$

Bearing in mind that each wire has two ends, we see that any wire used must have a length of at least sixty times the diameter, and temperature observations should be restricted to the central portion of such a wire.

There are two ways in which the temperature of the central portions of a wire heated by an electric current can be determined. In the first place the wire can act as its own resistance thermometer and the effect of the temperature gradient along the leads can be eliminated by measuring the difference in the resistance of two wires of unequal length, the shorter having a length of at least sixty diameters. In the other method a small auxiliary thermocouple is welded on to the centre of the hot wire and serves to measure directly the temperature difference between the wire and the liquid, one junction of the couple being on the wire and the other in the liquid. This latter method has proved particularly useful, but a few peculiar precautions are necessary. In the first place the thermocouple wires can produce additional lead losses, and for this reason they should be made of wire finer than the hot wire. In the second place it is impossible to make the weld without changing the local diameter of the centre

of the wire, so that the d to be inserted in equation (9) is a little uncertain. However, the instrument can always be calibrated by measurement in a liquid of known thermal conductivity.

When the temperature of the hot wire is measured by means of a small thermocouple it is preferable to use a wire of a metal such as constantan, which has a negligible temperature coefficient of resistance, so that the heat lost is simply proportional to the square of the current flowing. If the instrument is to be used for measuring relative conductivities there is no need to evaluate the proportionality factor. The thermocouple can be connected directly to a low resistance galvanometer and there is no need to estimate θ in units of temperature. The galvanometer readings are approximately directly proportional to θ . In operation therefore the heating current divided by the square root of θ (or the galvanometer reading) is plotted against the sixth root of θ . The extrapolated intercept at zero θ is directly proportional to the square root of the thermal conductivity of the liquid. Furthermore the slope of the line obtained from the one instrument in different liquids is directly proportional to the sixth root of the convection moduli. We have therefore a method of obtaining both the thermal conductivity and the convection modulus for an unknown liquid from a few very simple measurements.

SUMMARY.

The existing data for the convective loss from heated horizontal cylinders has been shown to fit the equation

$$\sqrt{\text{Nu}} = 0.63 + 0.35 \sqrt[6]{\text{Gp}}$$

over a range of 10^{14} for Gp, which here is written for the product of the Grashof and the Prandtl numbers. Nu refers to the Nusselt number.

The limiting value of Nu for very low values of Gp becomes

$$\lim_{\text{Gp} \rightarrow 0} \text{Nu} = 0.40$$

and from this limiting value the thermal conductivity can be obtained.

A heated alloy wire with a small thermocouple welded to the centre provides a means of studying the heat loss from a body of standard dimensions in different fluids. By plotting the quotient of the heating current by the root of the temperature rise versus the sixth root of the temperature rise, a straight line may be obtained. The intercept of this line is directly proportional to the root of the thermal conductivity of the liquid concerned and the slope to the sixth root of the convection modulus.

The most suitable dimensions for the hot wires are discussed in terms of the accuracy of extrapolation and the loss of heat by conduction along the leads.

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QUATERNARY ARSONIUM SALTS AND THEIR METALLIC CO-ORDINATION COMPOUNDS.

PART II. CADMIUM.

By F. P. DWYER, M.Sc.,
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and R. S. NYHOLM, M.Sc.

Manuscript received, October 11, 1944. Read, November 1, 1944.

Following on the investigation of the use of the quaternary arsonium iodides for the micro-detection of bismuth, reported in a previous communication, it was decided to examine the possibility of using them in a similar capacity for cadmium.

The micro reagents for the detection of cadmium depend either upon the formation of sparingly soluble complexes of the type R_2CdI_4 , for which allyl iodide hexammine (Evrard, 1929), β -naphthoquinoline (Berg and Wurm, 1927), phenyl trimethyl ammonium iodide (Pass and Ward, 1933) and ferrous 2, 2' dipyridyl (Feigl, 1943) have been suggested; the formation of coloured cadmium hydroxide lakes with diphenyl carbazide (Feigl and Neuber, 1923), its nitro derivative (Heller and Krumholtz, 1929), or p-nitrobenzenediazoaminoazobenzene (Dwyer, 1937); or finally the precipitation of the sparingly soluble salt of 3-nitro-4-hydroxy-phenyl arsonic acid (Pavelka and Kolmer, 1930). The iodide complexes will not in general detect less than 10 γ of Cd/ml., while some are less sensitive, and interference occurs with antimony, bismuth, lead, mercury, silver and copper, owing to the formation of similar complexes or the precipitation of the iodide of the metal. Among the cadmium hydroxide lakes, p-nitrobenzenediazoaminoazobenzene is by far the most sensitive, but does not lend itself to quantitative estimation, and may be regarded as too sensitive for normal analytical work.

The arsonium reagents described in this paper, whilst they also depend on the formation of complex iodides and hence suffer from the usual interference by the other metals, have the advantage of being extremely insoluble, in most cases, and in the best two reagents are twenty times as sensitive as those previously available.

As in the case of bismuth, two series of methyl aryl tetraiodo cadmium compounds have been prepared, and the effect of the substituent groups in the arsonium radical on the properties of the resultant compounds studied, with special reference to the sensitivity of the reaction.

The latter two members of both the phenyl and p-tolyl series are insoluble in water, while the first member of each series is sparingly soluble in cold water and readily soluble in hot. The compounds are soluble in hot acetone and alcohol and may be crystallised in white monoclinic plates.

In both series the melting points first fall, then rise, as the molecular weights increase.

The sensitivity of the reagents increased with the molecular weight, owing to the fact that it depended on one factor only, namely the solubility of the co-ordination compound, which decreased as the molecular weight increased.

During the examination of the sensitivity of the reaction, it was noted that cadmium could be estimated by turbidometric comparison with solutions of known cadmium concentrations in the presence of ten thousand times the amount of zinc.

The highest sensitivity obtained was 0.2 γ /ml. with p-tolyl₃ MeAsI, which is considerably higher than any reagent with the exception of p-nitrobenzene-diazoaminoazobenzene. Since the compounds contain less than 10% Cd, and since at concentrations of the order of 10 γ Cd/ml. the complexes are formed as very fine suspensions which coagulate very slowly, it is proposed to investigate the compounds for the gravimetric and nephelometric estimation of cadmium, for which suitable reagents are still required.

EXPERIMENTAL.

Bis triphenylmethylarsonium tetra-iodo cadmium. (C₆H₅)₃MeAsI (1 gm.), potassium iodide (1 gm.) and sulphuric acid (0.5 ml.) were dissolved in water (400 ml.) with warming. To this solution was added in a thin stream with stirring, a solution of cadmium sulphate (equivalent to 0.1 gm. of cadmium). The arsonium tetra-iodo compound separated as a fine white milky precipitate, which coagulated on continued stirring, leaving the supernatant liquid quite clear and colourless. The crystalline compound was filtered quite readily with suction, washed twice with 100 ml. of N/2 hydrochloric acid, then with distilled water, dried with suction and finally in the desiccator over calcium chloride.

The compound was not hydrolysed by boiling with water, but hot N/2 ammonium hydroxide decomposed it chiefly to diammine cadmium iodide.

The compound was analysed as follows: The iodine was estimated by the method of Dwyer and Nyholm (1942). Arsenic was estimated by fuming with sulphuric acid and potassium nitrate to remove organic matter. Traces of nitrous acid were removed with urea, and the arsenic acid, after reduction with sulphurous acid, estimated in the usual way with iodine. Cadmium was estimated by electrolysis from a cyanide solution after removing organic matter as before.

The other compounds (Table 1) were prepared and analysed similarly.

Found: As=10.8%; Cd=8.36%; I=39.5%. Calculated for ((C₆H₅)₃(CH₃)As)₂(CdI₄): As=11.1%; Cd=8.36%; I=40.2%.

Sensitivity. The cadmium solutions were prepared from purified 3CdSO₄ · 8H₂O prepared as a stock solution containing 1,000 γ Cd/ml. which was 1N with respect to H₂SO₄. This solution was diluted as required with distilled water.

TABLE 1.

Compound.	Melting Point.	Iodine Found.	Iodine Theoretical.	Sensitivity. γ Cd./ml.
((C ₆ H ₅) ₃ (CH ₃)As) ₂ (CdI ₄) ¹	189° C.	49.5%	50.1%	200.0
((C ₆ H ₅) ₃ (CH ₃)As) ₂ (CdI ₄)	173° C.	44.4%	44.6%	0.7
((C ₆ H ₅) ₃ (CH ₃)As) ₂ (CdI ₄)	179° C.	39.5%	40.2%	0.3
((C ₆ H ₅) ₃ (CH ₃)As) ₂ (CdI ₄)	188° C.	47.9%	48.7%	200.0
((C ₆ H ₅) ₃ (CH ₃)As) ₂ (CdI ₄)	128° C.	41.7%	42.5%	0.7
((C ₆ H ₅) ₃ (CH ₃)As) ₂ (CdI ₄)	203° C.	37.0%	37.8%	0.2

Where C₆H₅=the p-tolyl radical.

C₆H₅=the phenyl radical.

¹ Burrows and Turner (1921).

SUMMARY.

The use of quaternary arsonium iodides for the micro-detection of cadmium has been investigated, and it has been shown that these compounds can be used to detect cadmium in a concentration of less than 1 γ of cadmium per millilitre of solution, tri-p-tolylmethylarsonium iodide giving a reaction down to 0.2 γ

Cd/ml. The reaction may be used in the presence of large amounts of zinc, which does not interfere.

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COMPLEXES OF FERRIC CHLORIDE WITH TERTIARY ARSINES.

By R. S. NYHOLM, M.Sc.

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The ease with which trivalent arsenic in tertiary arsines passes to the four-covalent state is well exemplified by the various complexes which arsines form with metallic salts. Complexes of several of the metals in Group VIII have already been described. Thus, Dwyer and Nyholm (1942-4) have studied the arsine complexes of the halides of rhodium and iridium, Burrows and Parker (1934) those of platinum, and finally Mann and Purdie (1936) similar compounds of palladium. The iron complexes described in this paper have been investigated in view of their expected similarity to the halogen bridge structures formed by rhodium and iridium.

Two series of compounds have been isolated, of empirical formulæ, $\text{FeCl}_3 \cdot 2 \text{ Arsine (I)}$ and $2\text{FeCl}_3 \cdot 3 \text{ Arsine (II)}$, but all attempts to isolate compounds of ferrous iron have proved fruitless. The outstanding property of the compounds was their ease of dissociation in water and acids. Because of this they were prepared from alcohol solution. Recrystallisation was often not possible, either because of the tendency for the compound to be thrown out as oil or to dissociation.

The complexes of diphenylmethylarsine were most closely investigated but similar compounds with other arsines were obtained. The compounds with the di-alkyl arsines took many weeks to crystallise out and were very difficult to purify. Owing to solubility relationships and ease of dissociation with other arsines, the two different complexes, (I) and (II), were obtained only with diphenylmethylarsine.

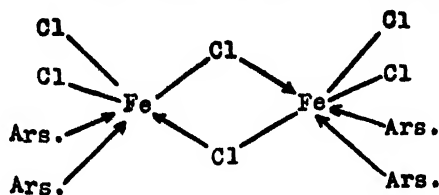
Compound (I), $2\text{FeCl}_3 \cdot 4\text{Ph}_2\text{AsMe}$, was obtained by treating an alcoholic solution of ferric chloride with excess of the arsine and purifying as below. The compound was only slightly soluble in water, the solution giving only a faint opalescence with silver nitrate but on boiling or treating the solution with nitric acid dissociation of the compound occurred with precipitation of all the chlorine. The substance was also less soluble in solvents and possessed a higher melting point (213°) than (II).

Compound (II), $2\text{FeCl}_3 \cdot 3\text{Ph}_2\text{AsMe}$, was much less stable than (I). It was prepared as for (I) using less arsine. This compound was readily soluble in water to form an electrically conducting solution, presumably due to structural breakdown, for the aqueous solution reacted readily with silver nitrate to precipitate silver chloride. Further, progressive dilution of the solution gave a reddish solution indicating hydrolysis of the ferric chloride. The substance was also more soluble in solvents and lighter in colour than (I).

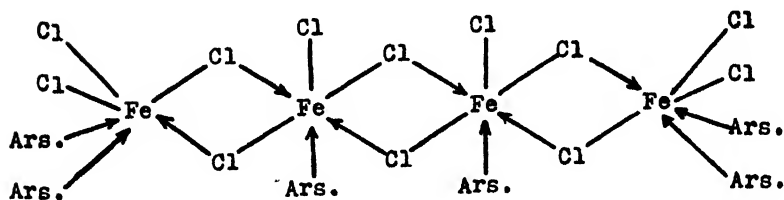
The weakness of the arsenic-metal bond in these compounds is not unusual. Burrows (1940), in a reference to arsine co-ordinated complexes of metallic salts, mentions that in some cases it was impossible to recrystallise the compounds without loss of arsine, while with others merely washing with ether caused loss of arsine.

The formula attributed to the complex (I) is to be expected since ferric chloride is frequently dimeric in organic solvents and the formulation merely involves the completion of the co-ordination number of six for ferric iron by the

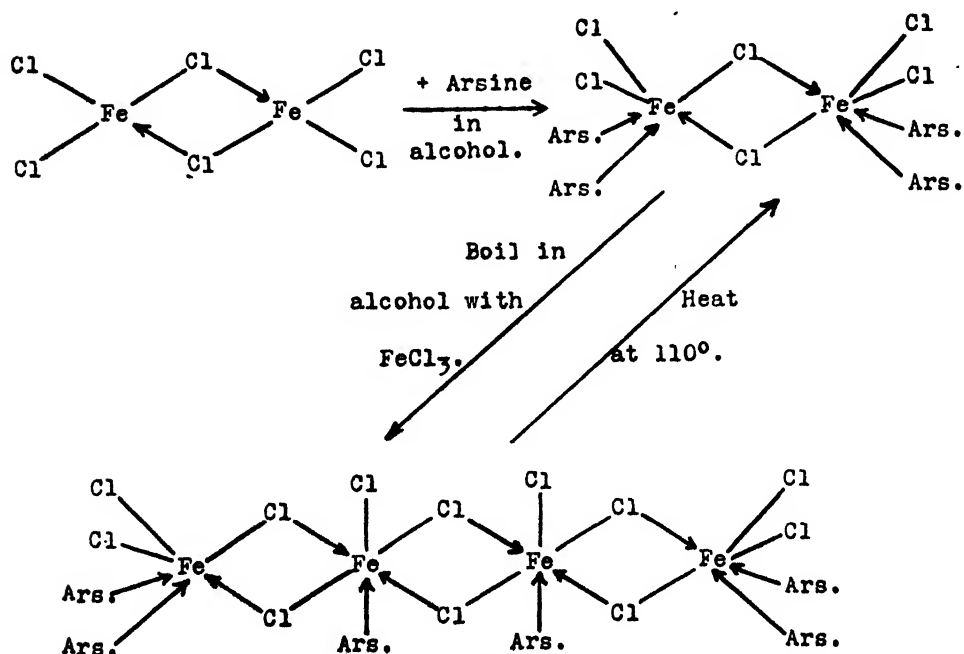
addition of four molecules of arsine to the Fe_2Cl_6 nucleus. The formula given to (II) is again necessary to complete the co-ordination number of six for iron. Previous examples of compounds in which four metal atoms have been joined by



(I)



(II)



halogen bridges include the polynuclear complexes of rhodium and tin with arsines, described by Dwyer and Nyholm (1942b), which were also characterized by their ease of dissociation. The ease of conversion of (I) to (II) by boiling with ferric chloride emphasizes their closely related formulæ.

EXPERIMENTAL.

Tetrachloro-tetrakis-diphenylmethylarsine-μ-dichloro-di-iron^{III}. (I.)

This compound is usually difficult to obtain free from (II). Ferric chloride hexahydrate (3 g.) in ethyl alcohol (25 ml.) was treated with diphenylmethylarsine (6 g.; i.e. excess arsine in the ratio 1 : 2½ mols) in alcohol (25 ml.) and the solution heated on the water bath for one hour, alcohol being gradually added to make up for evaporation. On cooling, the solution was left to stand and after some days brown crystals melting at 213° were obtained. Frequently compound (II) was co-precipitated, purification being effected by dissolving all in acetone and fractionally precipitating with alcohol, the required complex being precipitated first.

The compound was also conveniently prepared as follows: 1 g. of the compound $2\text{FeCl}_3 \cdot 3\text{Ph}_2\text{AsMe}$ (II) was heated for one hour at 110° on a watch glass. After melting a brown, vitreous residue was left which on cooling was recrystallised from acetone and alcohol. This reaction is of interest in that above the melting point, compound (II) dissociated with the splitting out of ferric chloride.

The pure compound crystallised in rods melting at 213°, and was only slightly soluble in water, the solution giving only a faint opalescence with silver nitrate until treated with nitric acid or boiled. It dissolved readily in acetone but was only slightly soluble in other organic solvents. A suspension of the complex in alcohol dissolved readily on boiling with ferric chloride solution due to change over to complex (II).

Found: Cl=16.4%, Fe=8.3%, As=21.7%.

Calculated for $[2\text{FeCl}_3 \cdot 4(\text{C}_6\text{H}_5)_2\text{AsCH}_3]_2$: Cl=16.4%, Fe=8.6%, As=23.0%.

Hexachloro-hexakis-diphenylmethylarsine-μ-dichloro-di-iron^{III}-μ-dichloro-di-iron^{III}-μ-dichloro-di-iron^{III}. (II.)

Ferric chloride hexahydrate (3 g.) in ethyl alcohol (25 ml.) were treated with diphenylmethylarsine (4 g.) (2 : 3 mols) in alcohol (25 ml.) and the solution heated on the water bath until about two-thirds of the alcohol had evaporated. The solution was then diluted to its original bulk and the process repeated. The solution was finally diluted to 50 ml. and allowed to stand. After two to three days yellow, cubic crystals were obtained and after washing with alcohol these were recrystallised from acetone and alcohol, the required compound being obtained as microcrystalline yellow plates melting at 93°. Often a small amount of compound (I) was first precipitated, for which reason the first fraction during recrystallisation was rejected.

The compound was extremely soluble in acetone, fairly soluble in glacial acetic acid and nitrobenzene and moderately soluble in alcohol; it dissolved slightly in, and could be recrystallised with difficulty from, benzene. It dissolved readily in water to form an electrically conducting solution indicating dissociation. On testing with hydrochloric acid and potassium ferrieyanide, this compound and all others gave no blue colour, indicating that the iron was present wholly in the ferric state. Molecular weight determinations in nitrobenzene showed marked dissociation.

Found: Cl=19.9%, Fe=10.4%, As=19.9%.

Molecular weight (cryoscopic in nitrobenzene)=477.487.

Calculated for $[2\text{FeCl}_3 \cdot 3(\text{C}_6\text{H}_5)_2\text{AsCH}_3]_2$: Cl=20.1%, Fe=10.6%, As=21.3%.

Molecular weight=2,114.

NOTE.—On occasions this compound has crystallised out with alcohol of crystallisation which could be removed by recrystallisation from benzene. The alcohol was confirmed by the iodoform test.

Tetrachloro-tetrakis-o-tolyldimethylarsine-μ-dichloro-di-iron^{III}. (Type I.)

This was the only compound similar to (I) obtained with a di-alkylarsine. After heating in the usual manner, o-tolyldimethylarsine (5 g.) and ferric chloride hexahydrate (3 g.) in alcohol (50 ml.) were allowed to stand. After some months brownish crystals melting at 115° were obtained which could not be recrystallised due to dissociation. The substance, although soluble

in water, did not precipitate silver chloride from silver nitrate till nitric acid was added, indicating similarity to compound (I). Sufficient compound for the Cl and As analyses only was obtained.

Found : Cl=19.2%, As=25.9%.

Calculated for $[2\text{FeCl}_3 \cdot 4\text{C}_7\text{H}_7\text{As}(\text{CH}_3)_3]$: Cl=19.2%, As=27.0%.

Hexachloro-hexakis-di-p-tolylmethylarsine-μ-dichloro-di-iron^{III}-μ-dichloro-di-iron^{III}-μ-dichloro-di-iron^{III}. (Type II.)

Di-p-tolylmethylarsine (4.5 gm.) and ferric chloride hexahydrate (3 g.) were allowed to react in 50 ml. alcohol in the usual manner and the mixture allowed to stand. After some days cubic crystals melting at 148° were obtained. Properties were similar to those of the corresponding diphenylmethylarsine complex except that recrystallisation was more difficult and solubilities generally were lower. Attempts to prepare a complex of Type I from this arsine, directly or indirectly, have proved a failure.

Found : Cl=19.1%, Fe=10.0%, As=18.6%.

Molecular weight (cryoscopic in nitrobenzene)=650,750.

Calculated for $[2\text{FeCl}_3 \cdot 3(\text{C}_7\text{H}_7)_2\text{AsCH}_3]_2$: Cl=18.7%, Fe=9.8%, As=19.7%.

Molecular weight=2,282.

Hexachloro-hexakis-dimethyl-p-tolylarsine-μ-dichloro-di-iron^{III}-μ-dichloro-di-iron^{III}-μ-dichloro-di-iron^{III}. (Similar to II.)

Ferric chloride hexahydrate (3 g.) and p-tolyldimethylarsine (4.5 g.) in alcohol (50 ml.) were heated as usual and allowed to crystallise. After some weeks yellow, monoclinic rods melting at 100-101° were obtained. This compound, as expected, was more difficult than with the di-aryl arsines to obtain pure and could not be recrystallised without passing to an oil. Even washing with ether tended to cause dissociation. The compound dissolved readily in solvents and gave the usual reaction with silver nitrate. It is of importance to note that if the original solution was too concentrated, heating caused the arsine to reduce the ferric chloride to ferrous chloride which was precipitated.

Found : Cl=23.8%, Fe=12.4%.

Calculated for $[2\text{FeCl}_3 \cdot 3\text{C}_7\text{H}_7\text{As}(\text{CH}_3)_2]_2$: Cl=23.33%, Fe=12.27%.

ANALYSIS.

Chlorine was determined by the distillation method of Dwyer and Nyholm (1942b). Iron provided some difficulty, being finally estimated by careful ignition of the complex with excess concentrated sulphuric acid. The iron remained as ferric oxide, some difficulty being experienced in preventing partial reduction to Fe_2O_3 , due to the reducing nature of other constituents, which tended to make results somewhat low.

Arsenic was determined by Kjeldahl decomposition of the complex with concentrated sulphuric acid and potassium sulphate and gravimetric estimation of the arsenic as As_2S_3 . Results were usually low, due partly to volatility of the arsine and partly to loss of arsenic as arsenious chloride. This difficulty was also encountered by Burrows and Parker (1934), whose results indicate that loss of arsenic was marked with chloride complexes.

SUMMARY.

The complexes of ferric chloride with tertiary arsines have been described. Two types, of empirical formulæ $\text{FeCl}_3 \cdot 2$ Arsine and $2\text{FeCl}_3 \cdot 3$ Arsine, have been isolated. Formulation of these complexes required halogen bridge structures if a covalency of six were assumed for iron. Similar structures have been ascribed to complexes of bivalent rhodium.

ACKNOWLEDGMENT.

The author wishes to acknowledge his indebtedness to Mr. G. J. Burrows, B.Sc., for suggesting this investigation, and to his colleague, Mr. F. P. Dwyer, M.Sc., for suggestions which have assisted in the formulation of compounds described in this paper..

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THE RESPONSE OF THE STERNAL INTEGUMENT OF *TRICHOSURUS VULPECULA* TO CASTRATION AND TO SEX HORMONES.

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University of Sydney.)

With Plate XIV.

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In a previous paper (Bolliger and Hardy, 1944) the highly glandular skin area over the sternum of *Trichosurus vulpecula* (the common Australian possum) and the distinctive brown hairs covering it, have been described and the significance of this region has been considered to be, mainly that of a male sex characteristic. This theory was found to be well supported after observing the effects of the following series of experiments on the sternal integument.

- (1) Castration of immature females and males.
- (2) Castration of sexually mature females and males.
- (3) Administration of female sex hormone to female and male castrates.
- (4) Administration of male sex hormones to female and male castrates.

(1) THE EFFECT OF CASTRATION ON THE STERNAL INTEGUMENT OF IMMATURE POSSUMS.

(a) *Females.* Three females were ovariectomised before they had reached sexual maturity. At the time of castration they were approximately 8 to 11 months of age and their sternal patches consisted either of exclusively grey hairs, or of grey with a small amount of light brown hair, or of grey with about an equal amount of light brown hairs. After castration these animals were observed for a period of 10 months, a period during which control animals of similar age changed from adolescence into sexual maturity, and developed the comparatively small but well defined sternal patch of the female.

The results of these experiments were a retarded and incomplete change from the grey sternal hair of the immature animal to the brown coloured hair of the quite mature female. For example, in the animal depicted in Figure 1, the majority of the sternal hairs were a light grey colour at the end of the period of observation and only the shaft of a few discreet hairs took on a light yellow brown colour, while in controls the greater part of the grey sternal peltage had changed into a brown colour.

(b) *Males.* Three males were castrated at the age of about six months. Two of these were subsequently given some injections of oestrogen and will therefore be mentioned again in paragraph 3 when dealing with the administration of female sex hormones to male castrates. At this stage it may, however, be stated that in all three animals no large, evenly brown or red-brown and oily sternal patch developed as was seen in controls. Moreover, the castrated

animal which received no oestrogens developed a permanent sternal streak consisting almost only of dry grey hairs. In a male castrated at the age of five months, a sternal streak consisting solely of dry grey hairs was present after the animal had attained maturity.

(2) THE INFLUENCE OF CASTRATION ON THE STERNAL INTEGUMENT OF MATURE POSSUMS.

(a) *Females*. Three females which had borne young were ovariectomised. During the period of observation of 10 months the animals became very obese but the sternal streaks were not markedly different from those of controls. All that could be said was that they were more yellow in colour and dry.

(b) *Males*. One fully grown but young male with many spermatozoa in its urine had its testes removed and then was given some oestrogen. Subsequently it was observed for a period of one year. During this period the sternal streak changed from its original reddish brown colour to a yellow-brown colour and decreased in size by about one-third. At the same time the light brown hairs on the thoracic region of the back ceased developing. As pointed out before, large areas of such hairs are typical for the adult male of two or more years of age, and are characterised by a salmon-red fluorescence if examined under ultra-violet light in the dark (Bolliger, 1944).

(3) ADMINISTRATION OF FEMALE SEX HORMONES TO FEMALE AND MALE CASTRATES.

(a) *Female*. A female was castrated at the age of about 10 months. At this stage only a few brown hairs had appeared in the centre of the otherwise grey sternal patch. One month after ovariectomy, oestradiol dipropionate was injected intramuscularly at about fortnightly intervals, starting with a dosage of 0.5 mg. and increasing it up to 1.6 mg. During a period of eight weeks a total of 4.2 mg. of oestradiol was administered and subsequently the animal was observed for four months. During this period of observation the number of brown hairs in the sternal area did not increase nor did they appear to become more deeply stained. There was, however, considerable secretion of pigment in the area of the pouch, as evidenced by strong brown coloration in and around the pouch. The animal also showed yellow discoloration in its face and to a lesser extent over the rest of the body.

(b) *Males*. The two animals in this series have already been referred to in a previous communication on the successful transformation of the scrotum of the castrated male into a marsupial pouch (Bolliger, 1944). One of these animals had been given a total of 1.8 gm. of stilboestrol over a period of four months before castration was performed and a total of 1.6 mg. of oestradiol dipropionate after orchidectomy at the age of six months. In addition to the formation of a pouch the sternal patch developed but poorly and at the age of one year and eleven months it consisted only of a yellow-brown area of hairs of about 1 cm. in length and 0.4 cm. in width which was hardly noticeable.

The other animal in this series has been described in detail (Bolliger, 1944) with regard to administration of oestrogen and its effects on the scroto-marsupium area and on the integument in general. The sternal area which has not yet been described in this experiment also showed a marked lack of development. About eighteen months after castration it consisted mainly of grey hairs which contained a core of brown and grey hairs of about 2 cm. in length and 0.5 cm. in width (Figure 3).

(4) ADMINISTRATION OF MALE SEX HORMONE TO FEMALE AND MALE CASTRATES.

In previous investigations it had been repeatedly observed, though not yet published, that the sternal colour-patch of normal females and of immature males which had been injected with testosterone (the male testicular hormone) increased in size and intensity. However, the results obtained from castrated animals proved more definite and will now be given in some detail.

(a) *Females.* A female ovariectomised at the age of eight months possessed, one month after castration, only a few light brown hairs in its grey sternal streak. At this date injections of testosterone were begun and for a period of six weeks 25 mg. of testosterone propionate were given weekly. After this, similar injections were given at fortnightly intervals and later at intervals of three weeks. Some response was already noticed a few days after the first injection and after four weekly administrations of the hormone most of the grey hairs of the sternal patch had assumed a rich brown colour. In a few more weeks the brown patch thus formed had acquired the dimensions and intensity of colour as seen in males of about similar age. Furthermore, the hairs in this region became slightly oily at this stage (Figure 2). After the injections had been continued for about four months the fur in general took on a yellow tinge.

For an additional period of four months the male appearance of the sternal area was retained by means of the administration of 25 mg. of testosterone propionate at intervals of three weeks. The injections were then discontinued and about six weeks after the last injection it was noticed that the sternal peltage had become dry and of a light yellow-brown colour. An increased number of grey hairs was also noticed.

Another animal in this group was also given six weekly injections of testosterone beginning one month after castration, and the brown coloration of the sternal area increased as described in the previous experiment. Then, however, injections were stopped and the sternal patch formed so far became dry and assumed a light brown colour. This still immature animal, however, otherwise proved to be resistant to further involutional changes for a considerable time. In the course of four months of observation only a comparatively small number of grey or white hairs had reappeared. After eight months the sternal area, as indicated by a mixture of fine, very light brown and light grey hairs, had decreased to about half of the area present immediately after the administration of testosterone and closely resembled that of the castrated female described in paragraph 1 (Figure 1).

(b) *Male.* The male used in this experiment, lasting for over two years, has already been referred to in connection with the transformation of the scrotum into a pouch as already mentioned in paragraph 3 of this paper. The possum was castrated at the age of six months and then was given a total of 5.5 mg. of oestradiol dipropionate over a period of four months. After an additional period of one year, during which no further injections of oestrogens were given, the scrotum transformed into a female marsupium and then finally reformed again to a very atrophic scrotum (Bolliger, 1944). At this stage the sternal area was found to consist mainly of grey hairs containing a small core (2×0.5 cm.) of light brown and grey hairs. In general, the colour streak then could in no way be compared with that seen in the male of similar age, i.e. two years. It was even considerably less marked than that seen in the normal female and resembled the sternal patch as it appeared in a female who had been castrated before reaching the age of puberty.

At this stage fortnightly injections of 25 mg. of testosterone propionate were begun. Soon after the second injection the predominantly grey sternal area was noticed to take on a superficial brown stain and some of the grey hairs

seemed to change colour. After six injections practically all the grey hairs had disappeared, being replaced by brown ones which in their totality formed a sternal area comparable to that seen in normal males of similar age. After further injections, parts of the white fur on the anterior aspect of the animal became stained a yellow-brown to form a broad "V", the limbs of the "V" originating near the axillæ and the apex extending caudally along the mid-line (Figure 4).

Six months after terminating the injections, the brown colour of the sternal hairs had again almost completely disappeared.

DISCUSSION.

The experiments described in paragraph 4 demonstrate that the full development of the sternal patch is mainly under the control of the testicular hormone. In its absence, i.e. after castration, it does not develop or only poorly so and on the administration of the crystalline male hormone testosterone, the typical sternal patch is restored in the castrated male. But also in the castrated female a male sternal patch is produced.

In the light of previous investigations (Bolliger and Hardy, 1944) this indicates that testosterone brings into marked activity the skin glands of this region and sufficient chromogen is formed, not only to dye practically all of these specific sternal hairs, but also to stain the surrounding fur. Furthermore, secretions from sebaceous and sudoriferous glands give the area a wet and oily appearance comparable to that seen in adult normal males.

No similar changes subsequent to the administration of testosterone have so far been described in other mammals. Changes somewhat comparable have been described in the English sparrow and some other finches. Castrates of both sexes of these birds have a permanently lightly coloured bill, but injections of male sex hormone bring on a blackening of this organ (Keck, 1934). Our marsupial, however, does not exhibit, to anything like the same degree, the marked colour changes seen during the breeding season in the normal male of the English sparrow, in which, on approach of the breeding season, the horn-brown colour of the bill alters to a jet black. The sternal area of the male of *Trichosurus vulpecula*, after it has been fully established, shows only slight seasonal changes. After castration it changes its colour from a rich brown or red-brown to a light yellow-brown in the course of several months.

In castrated females the sternal patch developed more slowly and less completely than in controls, which may indicate that the ovary exerts a definite influence on the development of this secondary male sex characteristic and which after removal of the gonads cannot be replaced by oestrogens. On the other hand, the administration of testosterone to the castrated female brings on the formation of a sternal patch with male characteristics, while the administration of oestrogens to castrated males has no characteristic influence on this area.

In a previous paper (Bolliger and Hardy, 1944), it has been pointed out that the morphology of the skin over the sternum was in general similar to that of the rest of the body and that the most important differences are of a quantitative nature in that both sebaceous and sudoriferous glands are very large and active in this area. Consequently, natural changes or changes brought on by experimental interference find a concentrated and exaggerated expression in this area, but these activities are also bound to occur on the rest of the body, though on a much smaller scale. In the present experiments this has been demonstrated in the change of the colour of the fur in general after the administration of testosterone. Changes in the peltage after castration and after the administra-

tion of oestrogens were also visible. They were also accompanied by changes in the general nature of the skin, such as thickness and toughness. These will be discussed on another occasion.

SUMMARY.

The brown sternal hairs of *Trichosurus vulpecula* are mainly a male sex characteristic. Castration, as well as castration plus administration of oestrogen, hinders their development in the male, but they can be fully developed subsequently by the administration of testosterone propionate.

In normal and castrated females, testosterone propionate brings on a patch of sternal fur of male dimensions and appearances.

In the female castration also retards the development of the small area of brown sternal hairs.

In fully grown animals of both sexes castration has comparatively little effect on the sternal fur.

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EXPLANATION OF PLATE.

Fig. 1.—Showing the grey sternal area containing only a few light brown hairs of a castrated female ten months after ovariectomy.

Fig. 2.—Showing the sternal area of a female of the same age and castrated at the same time as that shown in Fig. 1. The brown male-like sternal fur was brought on by the administration of testosterone.

Fig. 3.—Male castrated at the age of about six months. Present age about two years. Note the small grey sternal patch which contains only a few light brown hairs.

Fig. 4.—The same animal as shown in Fig. 3 after the repeated administration of testosterone propionate. Note the large typically male sternal patch, as well as the stain on the thoracic fur originating near the axillæ and forming a broad "V".

For appearance of sternal areas in normal females and males, see previous paper in this volume (Bolliger and Hardy, 1944).



Fig. 1.



Fig. 2.



Fig. 3.



Fig. 4.

A POLAROGRAPHIC STUDY OF THE ISOMERIC CHROMIUM SULPHATES.

By J. B. WILLIS, B.Sc.

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It is well known that several chromium salts, notably the chloride and sulphate, exist in two forms, violet and green in colour respectively. After much empirical work on the part of many chemists, Werner and Gubser (1901) finally settled the constitution of the violet and green chlorides as $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$. The chemistry of the various sulphates is rather more complicated; but the violet variety has the structure $[\text{Cr}(\text{H}_2\text{O})_5]_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$, and the various green forms are supposed to contain ions in which two or more molecules of water have been replaced by sulphate radicles.

The present investigation was undertaken to find out what differences in polarographic behaviour of such salts could be observed, and to determine what effect dilution had on the ion-species.

The chlorides were not studied owing to the great difficulty encountered in preparing pure specimens of the violet form, but the sulphates were used instead. These have the advantage of having been studied polarographically by Demassieux and Heyrovsky (1929). The present work is thus to some extent a revision of the results obtained by these authors, which is rendered necessary by the fact that at the time of their work very little was known of the theory of the polarograph, and some of the conclusions they drew are of doubtful validity. The concept of half-wave potential had not been developed at that time and the investigators used instead the tangent potential. Polarograms were often taken without any supporting electrolyte.

THEORY.

The number of electrons, n , in each reduction step may be found with the help of the Ilkovic equation, provided the diffusion coefficient of the reducible metal ion is known. This can easily be determined in the way described by Kolthoff and Lingane (1941). The n value so obtained is independent of the reversibility of the reduction. For details of such calculations, see Willis (1944).

By finding the equation of the polarographic wave, n may be evaluated if the reduction is reversible. The reversibility or otherwise of the reduction immediately becomes apparent when the calculation is carried out. If E is the potential and i is the current at any point of the step and i_d the diffusion current, then the plot of $\log \frac{i}{i_d - i}$ against E , called the log plot, is a straight line, provided the reduction is reversible, and has a reciprocal slope of $\frac{0.059}{n}$ volts. Thus a log plot of reciprocal slope 0.059 v., indicates a reversible one-electron reduction, one of slope 0.030 v., a reversible two-electron reduction, etc. If the slope does not fall near these values, or if the log plot is not a straight

line, the reduction is irreversible, and the half-wave potential, $E_{1/2}$, is usually found to be more negative than in the case of a reversible reduction process.

THE WORK OF DEMASSIEUX AND HEYROVSKY.

These authors studied violet chromium chloride, violet chromium sulphate, and potassium and rubidium chrome alums at various dilutions, both with and without the addition of N potassium sulphate. They used the tangent method for the estimation of reduction potentials, and did not measure the half-wave potentials. The former are shifted by $\frac{0.059}{n}$ volts to a more positive value for a ten-fold increase in concentration, while the latter remain unaltered by variations in the concentration of reducible ions. From the fact that the shift of the tangent potential in the simple chloride and sulphate was not in accordance with the theoretical values given above, they concluded that in these solutions the ion-species changed on dilution and that the degree of hydration of the ions was greater at higher dilutions. In the case of the alums, however, the variation was small and more regular, which they interpreted as signifying no change of ionic species on dilution.

EXPERIMENTAL.

The experimental arrangements were similar to those used in a previous investigation (Willis, 1944). All measurements were carried out at 25° C. and the air removed from the solutions with purified nitrogen. Potentials are given relative to that of the saturated calomel electrode (S.C.E.) and are corrected for the potential drop across the polarographic cell. The supporting electrolyte used throughout was N potassium sulphate.

The substances used were analysed for chromium in the following way :

A known weight of the substance was dissolved in water and made alkaline with sodium hydroxide. Excess hydrogen peroxide was added and the solution boiled until oxidation was complete and all excess hydrogen peroxide had been decomposed. It was then acidified with sulphuric acid, made up to a known volume, and titrated with 0.1 N ferrous ammonium sulphate in the usual way, using potassium ferricyanide as an external indicator.

The violet chromium sulphate was prepared by the method of Weinland and Krebs (1906).

Found : Cr=14.8%. Calculated for $\text{Cr}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$: Cr=14.8%.

The chromium alum was May and Baker's preparation.

Found : Cr=10.4%. Calculated for $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$: Cr=10.5%.

The green chromium sulphate was May and Baker's "Chromium Sulphate".

Found : Cr=19.2%. Calculated for $\text{Cr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$: Cr=19.4%.

RESULTS.

Violet Chromium Sulphate.

Two steps were obtained, the height of the second being rather more than twice that of the first. This is apparently due to the simultaneous discharge of hydrogen ion with the chromous ion, since chromic salts are appreciably hydrolysed. The hydrogen step proper begins immediately after the conclusion of the second step, and in the strongest solution studied (0.02 M in chromium), the second step and the hydrogen step merged into one. No maxima were found, in contrast to the case of chrome alum (see below).

Application of the Ilkovic equation, using the conductivity data of Graham (1912) for violet chromium sulphate, gave n values of 1.0 and 2.3 respectively. As mentioned above, the second step is abnormally high owing to the simultaneous discharge of hydrogen.

The half-wave potential of the first step remains constant with dilution, having the value -1.041 v. The log plot is a straight line of reciprocal slope 0.058 v., which indicates a reversible one-electron process.

The half-wave potential of the second step is not quite constant with dilution, but shows a small drift towards more positive values as the dilution increases. These potentials are difficult to reproduce with accuracy owing to the proximity of the hydrogen step. The significance of this drift is not apparent. The log plot of the second step is a straight line with a reciprocal slope of 0.034 v., which seems to indicate a reversible two-electron reduction.

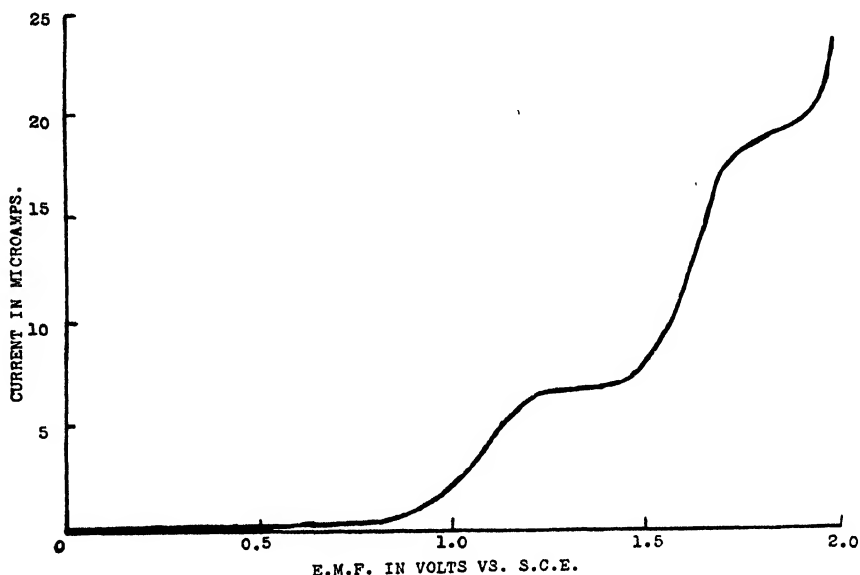


Fig. 1.—0.002 M violet chromium sulphate in N potassium sulphate.

According to Kolthoff and Lingane (1941) the half-wave potential of a step due to the discharge of a metal insoluble in mercury should theoretically shift by $\frac{0.059}{n}$ volts in a *negative* direction for a ten-fold decrease of concentration, but it is doubtful whether any metal is sufficiently insoluble in mercury for the theory to apply more than qualitatively. The same theory also requires that the wave should start vertically from the voltage axis, but in no case does such a phenomenon seem to occur. Iron and chromium, which are usually considered insoluble in mercury, are discharged in the ordinary way and give the normal type of step. According to determinations by the present author, the log plot of the ferrous ion step in M potassium chloride yields a straight line with a reciprocal slope of 0.041 v.

Chrome Alum.

Here again two steps were observed, the second being a little more than twice the first, and the discharge of the supporting electrolyte followed close on the second step. In the second step there was a slight maximum in solutions stronger than 0.04M, which disappeared in more dilute solutions. Gelatine did not suppress the maximum, but shifted the half-wave potential of the *first* step by -0.14 v. Methyl red had no effect on the maximum. The measurements were made without the addition of any maximum suppressor.

The height of each step was proportional to the concentration, and the ratio of the height of the second step to that of the first was 2.05 : 1. Application of the Ilkovic equation using the conductivity data of Jones and Mackay (1897)

for chrome alum gave n values of 0.78 and 1.64 for the first and second step respectively.

The half-wave potentials remained constant with dilution at -1.035 v. and -1.630 v. respectively. The log plot of the first step was a straight line with a reciprocal slope of 0.054 v., which indicates a fairly reversible one-electron reduction. The second step gave a straight line with a slope of 0.041 v., which indicates a not perfectly reversible reduction process.

It is well known that violet chrome alum solutions if heated to about 70° change colour to green. A $0.01M$ solution of violet chrome alum in N potassium sulphate was refluxed on a boiling water-bath for five hours and a polarogram taken after it had cooled. The polarogram closely resembled that of a $0.01M$ solution of green chromium sulphate, but the second step was somewhat better defined and there was no maximum. The $E_{1/2}$ values for the two steps were -1.257 and -1.608 v. respectively.

Green Chromium Sulphate.

The curves obtained were somewhat ill-defined and not always perfectly reproducible. Two steps were in general discernible, but they were rather close together, which made accurate measurement difficult. During the second step the dropping of the mercury electrode became uneven, and maxima were often found, making the shape of the step very irregular. In the more dilute solutions the curves were a little better defined.

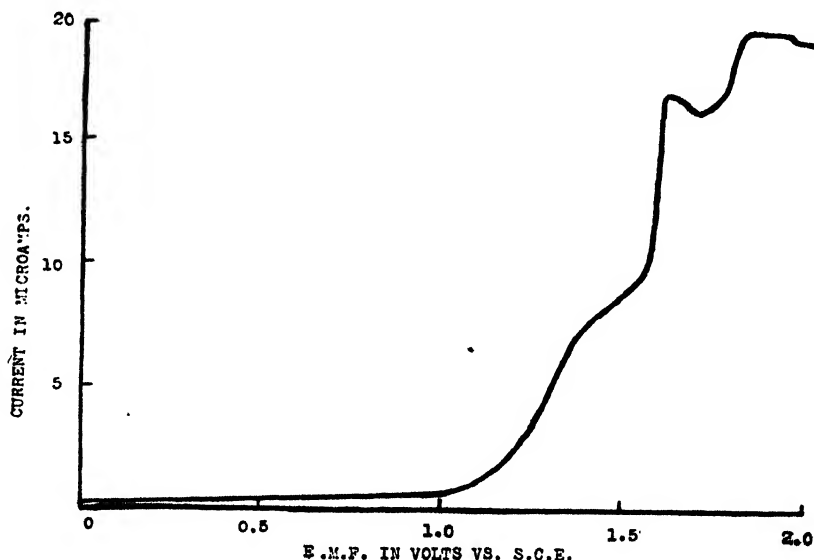


Fig. 2.— 0.002 M green chromium sulphate in N potassium sulphate.

The first step occurred at -1.258 v., constant with dilution, and the step-height was proportional to the concentration. The step was much less steep than in the case of the violet sulphate and the log plot was not a straight line. This indicates an irreversible reduction. The second step occurred at about -1.58 v. but in the more concentrated solutions the curves were so irregular that measurement of the half-wave potential became almost impossible. The shape of the steps was not improved by allowing the solutions to stand for several days to attain equilibrium.

TABLE OF HALF-WAVE POTENTIALS.

	1st Step.	2nd Step.
<i>Violet chromium sulphate</i>		
0.02M	-1.035 v.	—
0.01	-1.037	-1.616 v.
0.004	-1.037	-1.603
0.002	-1.035	-1.590
0.001	-1.046	-1.570
0.0005	-1.058	-1.564
Average	-1.041 v.	
<i>Chrome alum.</i>		
0.02M	-1.032 v.	-1.631 v.
0.01	-1.031	-1.639
0.004	-1.040	-1.638
0.002	-1.035	-1.627
0.001	-1.044	-1.617
Average	-1.035 v.	-1.630
0.01M after heating ..	-1.257 v.	-1.608 v.
<i>Green chromium sulphate.</i>		
0.02M	-1.255 v.	-1.53 v.
0.01	-1.256	-1.53
0.004	-1.254	-1.56
0.002	-1.263	-1.584
0.001	-1.261	-1.578
Average	-1.258 v.	

DISCUSSION.

From the fact that the half-wave potential of the first step of the polarogram of violet chromium sulphate is constant with dilution, and from the fact that the step-height is proportional to the concentration it is deduced that in N potassium sulphate no change of ion-species takes place on dilution over the range 0.02M–0.0005M.* Whether such a change takes place in the absence of potassium sulphate cannot be determined polarographically, but Werner and Gubser (1901) state that the conductivity of the violet sulphate behaves normally on dilution. A similar conclusion may be drawn about chrome alum. From the fact that E_1 for the reduction $\text{Cr}^{\text{III}} \rightarrow \text{Cr}^{\text{II}}$ is the same in both cases, it is deduced that the same ion-species is being reduced in both solutions. The non-existence of an equilibrium mixture of ions may also be deduced from the reversibility of the first step: a mixture of two interconvertible forms would certainly give rise to a slow electrode process, whose rate would be governed by the rate of inter-conversion of the two forms.

Conductivity measurements by Jones and Mackay (1897) show that in aqueous solution at a concentration of about 0.005M and above, chrome alum does not behave as an ideal mixture of chromium sulphate and potassium sulphate, but that there appears to be some interaction of the components, with the result that the conductivity is markedly lower than the arithmetic mean of that of the two salts at the same concentration. It was also found that made-up mixtures of chromium sulphate and potassium sulphate at high concentrations did not have the same conductivity as the alum. Now the polarographic measurements on both the violet chromium sulphate and chromium alum were carried out in a large excess of potassium sulphate, i.e. in the case of the simple

* The ultra-violet absorption spectra of the 0.01 and 0.001 M solutions have been taken in this laboratory by Mr. J. A. Friend, who finds no difference between them.

sulphate we have what is really a made-up mixture of chromium sulphate and potassium sulphate. A slight difference in the polarograms might be expected; and indeed the log plot of the first step shows that the reduction of the simple sulphate is more reversible than that of the alum. This is explicable on the grounds that before reduction of Cr^{III} to Cr^{II} can take place in the alum, the ion present, i.e. $[\text{Cr}(\text{SO}_4)_2]^-$ must dissociate into Cr^{+++} and 2SO_4^{--} ; if this process is not instantaneous, the reduction cannot be perfectly reversible.

Demassieux and Heyrovsky state that "the steps are steeper in the alum than in the simple sulphate, indicating a slowness of electrochemical reduction in the latter attributable to the equilibrium between the green and violet forms". However, the mathematical analysis of the steps, as just pointed out, shows the reverse to be true.

The E_1 value for the $\text{Cr}^{+++} \rightarrow \text{Cr}^{++}$ reduction might be thought to be identical with the classical redox potential for this process, but this is not so. E_1 is -1.04 v. vs. the S.C.E., i.e. -0.79 v. vs. the normal hydrogen electrode, whereas the classical redox potential is about -0.40 v. (Grube and Schlecht, 1926). It must be remembered however that the classical redox potential was determined without a supporting electrolyte, whereas the polarographic potentials were determined in the presence of a very large excess of an electrolyte, which has a considerable influence on the activity of the ions.

With regard to the green sulphate it can be said that the first stage is the reduction of an ion which does not vary with the concentration. The potential required is 0.22 v. more negative than that required for the violet sulphate, which is explicable on the grounds that a considerable over-voltage is necessary in the reduction of the green sulphate. The first step may be due to the reduction of an ion such as $[\text{Cr}(\text{H}_2\text{O})_4\text{SO}_4]^+$. Of the second step little can be said except that it corresponds to some complex reactions, possibly of a type which is not recorded satisfactorily by the polarograph.

SUMMARY.

In the polarographic reduction of violet chromium sulphate and of chrome alum in N potassium sulphate the same ion is reduced in both cases. The ion is probably $[\text{Cr}(\text{H}_2\text{O})_6]^{+++}$, since dilution does not alter the half-wave potentials of the reduction steps, as would be expected if a change of ionic species occurred. In the alum the reduction seems to be a little less reversible than in the simple sulphate. This fact might be explained by assuming that ions such as $[\text{Cr}(\text{SO}_4)_2]^-$ are present, and that these have to dissociate before undergoing reduction. The reduction takes place in two stages which are shown to be due to the processes $\text{Cr}^{\text{III}} \rightarrow \text{Cr}^{\text{II}}$ and $\text{Cr}^{\text{II}} \rightarrow \text{Cr}$ respectively.

The green sulphate undergoes irreversible reduction to a substance which seems to decompose in some complex way which is not satisfactorily recorded by the polarograph. The potential of the first step, however, does not change with dilution, which indicates that the ionic species remains the same throughout.

The solution of the violet alum when heated changes to green and gives a polarogram similar to that of the green sulphate.

ACKNOWLEDGMENTS.

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THE VIBRATIONS OF SQUARE MOLECULES.

PART II. THE VIBRATION FREQUENCIES OF PLANAR AB_3C_2 (TRANS) MOLECULES.

By ALLAN MACCOLL, M.Sc.

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INTRODUCTION.

In Part I (Maccoll, 1943) expressions for the symmetry co-ordinates and vibration frequencies of the planar AB_4 molecule (D_{4h}) were obtained. It is of interest to examine the case of the planar trans AB_3C_2 molecule in which the symmetry has been reduced to V_h . Expressions for the frequencies of the vibrations symmetrical to C_2^z have been obtained to a valence force approximation by Bernstein (1938).

THE SYMMETRY CO-ORDINATES.

The classes of symmetry operations of the group V_h are :

- (a) The identity operation E.
- (b) Twofold rotations around the z axis, C_2^z .
- (c) Twofold rotations around the y axis, C_2^y .
- (d) Twofold rotations around the x axis, C_2^x .
- (e) Inversion in the centre of symmetry, I.
- (f) Reflection in the xy plane, σ_{xy} .
- (g) Reflection in the xz plane, σ_{xz} .
- (h) Reflection in the yz plane, σ_{yz} .

The symmetry elements are shown in Fig. 1. As in Part I, the reducible representation of the molecular vibrations can be expressed in terms of the irreducible representations of V_h .

$$\Gamma = 2A_{1g} + B_{1g} + 2B_{1u} + 2B_{2u} + 2B_{3u}.$$

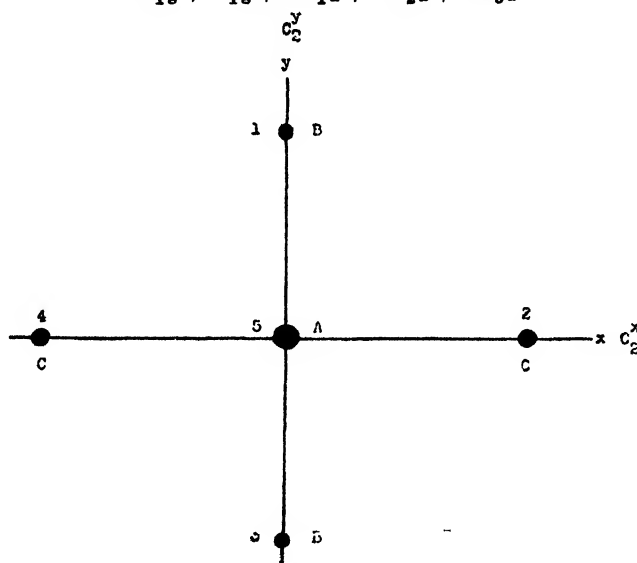


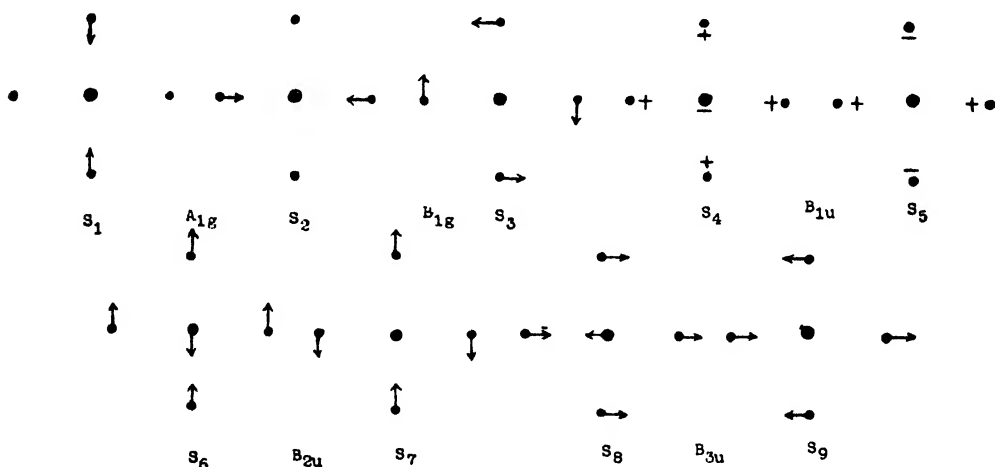
Fig. 1.—Coordinate axes of the AB_3C_2 molecule.

The transformation properties of the symmetry co-ordinates are shown in Table I (cp. Wilson, 1934).

TABLE 1.

Class.	No. Vibrations.	Co-ord.	Symmetry with respect to								Active in		Polarisation.
			E	C_2^z	C_2^y	C_2^x	I	σ_{xy}	σ_{xz}	σ_{yz}	Raman.	I.R.	
A_{1g}	2	S_1 S_2	+	+	+	+	+	+	+	+	yes	no	P
B_{2u}	2	S_6 S_7	+	-	-	+	-	+	+	-	no	yes	—
B_{1g}	1	S_3	+	+	-	-	+	+	-	-	yes	no	D
B_{1u}	2	S_4 S_5	+	+	-	-	-	-	+	+	no	yes	—
B_{2u}	2	S_6 S_7	+	-	+	-	-	+	-	+	no	yes	—

It is seen that from symmetry considerations the secular equation of the ninth degree can be factored into one linear and four quadratic factors. So one symmetry co-ordinate S_3 can be set up which is also a normal co-ordinate, while $S_1, S_2; S_4, S_5; S_6, S_7$; and S_8, S_9 have to be linearly combined to give the corresponding normal co-ordinates. The symmetry co-ordinates are shown in Fig. 2.

Fig. 2.—Vibrational symmetry coordinates of the AB_2C_2 molecule.

THE KINETIC AND POTENTIAL ENERGIES AND VIBRATION FREQUENCIES.

It is now possible to write down analytical expressions for the symmetry co-ordinates. As in Part I, these will be derived in terms of the mass reduced internal cartesian co-ordinates (ξ_1, η_1, ζ_1) of the particles subject to the condition that they are normalised and orthogonal both to themselves and to the co-ordinates (1) representing the infinitesimal translations and rotations of the molecule.

These latter are :

$$\begin{aligned} Q\rho &= m^{\frac{1}{2}}(\rho_1 + \rho_3) + m'^{\frac{1}{2}}(\rho_2 + \rho_4) + M^{\frac{1}{2}}\rho_5 \\ \text{where } \rho &= \xi, \eta, \zeta. \\ Q\omega_x &= \zeta_1 - \zeta_3 \dots\dots\dots (1) \\ Q\omega_y &= -\zeta_2 + \zeta_4 \\ Q\omega_z &= m a^{\frac{1}{2}}(-\xi_1 + \xi_3) + m' a'^{\frac{1}{2}}(\eta_2 - \eta_4). \end{aligned}$$

The analytical expressions for the symmetry co-ordinates can now be written down.

They are :

$$\begin{aligned} S_1 &= 2^{-\frac{1}{2}}(-\eta_1 + \eta_3) \\ S_2 &= 2^{-\frac{1}{2}}(-\xi_2 + \xi_4) \\ S_3 &= [2(ma^2 + m'a'^2)]^{-\frac{1}{2}}[m'^{\frac{1}{2}}a'(-\xi_1 + \xi_3) + m^{\frac{1}{2}}a(-\eta_2 + \eta_4)] \\ \left. \begin{aligned} S_4 \\ S_6 \\ S_8 \end{aligned} \right\} &= [2(m+m')(2m+2m'+M)]^{-\frac{1}{2}}[(mM)^{\frac{1}{2}}(\rho_1 + \rho_3) + (m'M)^{\frac{1}{2}}(\rho_2 + \rho_4) \\ &\quad - 2(m+m')\rho_5] \dots\dots\dots (2) \\ \left. \begin{aligned} S_5 \\ S_7 \\ S_9 \end{aligned} \right\} &= [2(m+m')]^{-\frac{1}{2}}[-m'^{\frac{1}{2}}(\rho_1 + \rho_3) + m^{\frac{1}{2}}(\rho_2 + \rho_4)] \end{aligned}$$

$$\text{where } \rho \begin{cases} = \xi & (S_8, S_9) \\ = \eta & (S_6, S_7) \\ = \zeta & (S_4, S_5) \end{cases}$$

$$\text{and } S_7 = -S'_7.$$

Since this transformation is orthonormal, the expressions for (ξ_1, η_1, ζ_1) in terms of the S_1 can be written down by interchanging the rows and columns in its matrix.

$$\text{The kinetic energy reduces to } 2T = \sum_{i=1}^9 \dot{S}_i^2 \dots\dots\dots (3)$$

while the most general potential function is :

$$2V = \sum_{i=1}^9 \frac{K_i}{\mu_i} S_i^2 + \frac{2K_{12}}{(\mu_1\mu_2)^{\frac{1}{2}}} S_1 S_2 + \frac{2K_{45}}{(\mu_4\mu_5)^{\frac{1}{2}}} S_4 S_5 + \frac{2K_{67}}{(\mu_6\mu_7)^{\frac{1}{2}}} S_6 S_7 + \frac{2K_{89}}{(\mu_8\mu_9)^{\frac{1}{2}}} S_8 S_9 \dots\dots\dots (4)$$

$$\text{where } \mu_1 = m, \mu_2 = m', \mu_3 = (mm')^{\frac{1}{2}}$$

$$\mu_4 = \mu_6 = \mu_8 = \frac{2M(m+m')}{2m+2m'+M}$$

$$\mu_5 = \mu_7 = \mu_9 = \frac{m+m'}{2}.$$

The solution of the secular equation then gives

$$v_3 = \frac{1}{2\pi c} \left(\frac{K_3}{\mu_3} \right)^{\frac{1}{2}}$$

and

$$v_{1,j} = \frac{1}{4\pi c} \left\{ \frac{K_1}{\mu_1} + \frac{K_j}{\mu_j} \pm \left[\left(\frac{K_1}{\mu_1} - \frac{K_j}{\mu_j} \right)^2 + \frac{4K_{1j}^2}{\mu_1\mu_j} \right]^{\frac{1}{2}} \right\}$$

where $i, j = 1, 2; 4, 5; 6, 7; \text{ or } 8, 9.$

THE POTENTIAL FUNCTION.

As in Part I, a valence force potential function, modified by the addition of cross terms, will be used.

This is given by :

$$\begin{aligned}
 2V = & k_r(\delta r_1^2 + \delta r_3^2) + k_{r'}(\delta r_2^2 + \delta r_4^2) \\
 & + 2k_{rr'}(\delta r_1 + \delta r_3)(\delta r_2 + \delta r_4) + 2k'_{rr} \delta r_1 \delta r_3 \\
 & + 2k'_{r'r'} \delta r_2 \delta r_4 + k_a a^2(\delta \alpha_1^2 + \delta \alpha_3^2) \\
 & + k_{\alpha'} a'^2(\delta \alpha_2^2 + \delta \alpha_4^2) + 2k_{\alpha\alpha'} a a'(\delta \alpha_1 + \delta \alpha_3)(\delta \alpha_2 + \delta \alpha_4) \\
 & + 2k'_{\alpha\alpha} a^2 \delta \alpha_1 \delta \alpha_3 + 2k'_{\alpha'\alpha'} a'^2 \delta \alpha_2 \delta \alpha_4 \dots \dots \dots (6) \\
 & + k_\beta a^2(\delta \beta_1^2 + \delta \beta_3^2) + k_{\beta'} a'^2(\delta \beta_2^2 + \delta \beta_4^2) \\
 & + 2k_{\beta\beta'} a a'(\delta \beta_1 + \delta \beta_3)(\delta \beta_2 + \delta \beta_4) + 2k'_{\beta\beta} a^2 \delta \beta_1 \delta \beta_3 \\
 & + 2k'_{\beta'\beta'} a'^2 \delta \beta_2 \delta \beta_4.
 \end{aligned}$$

On expressing (6) in terms of the S_i , the following relations are obtained between the force constants of the general potential function (4) and those of the valence force function (6) :

$$\begin{aligned}
 K_1 &= k_r + k'_{rr} \\
 K_2 &= k_{r'} + k'_{r'r'} \\
 K_3 &= \frac{1}{(mm')^{\frac{1}{2}}(ma^2 + m'a'^2)} \{a'^2 m'^2 (k_\alpha + k'_{\alpha\alpha}) + a^2 m^2 (k_{\alpha'} + k'_{\alpha'\alpha'}) - 4aa' m m' k_{\alpha\alpha'}\} \\
 K_4 &= 2(k_\beta + k'_{\beta\beta} + k_{\beta'} + k'_{\beta'\beta'} + 4k_{\beta\beta'}) \\
 K_5 &= \frac{1}{2mm'} \{m'^2 (k_\beta + k'_{\beta\beta}) + m^2 (k_{\beta'} + k'_{\beta'\beta'}) - 4mm' k_{\beta\beta'}\} \\
 K_6 &= 2(k_r - k'_{rr} + k_{\alpha'} - k'_{\alpha'\alpha'}) \dots \dots \dots (7) \\
 K_7 &= \frac{1}{2mm'} \{m'^2 (k_r - k'_{rr}) + m^2 (k_{\alpha'} - k'_{\alpha'\alpha'})\} \\
 K_8 &= 2(k_{r'} - k'_{r'r'} + k_\alpha - k'_{\alpha\alpha}) \\
 K_9 &= \frac{1}{2mm'} \{m^2 (k_{r'} - k'_{r'r'}) + m'^2 (k_\alpha - k'_{\alpha\alpha})\} \\
 K_{12} &= 2k_{rr'} \\
 K_{45} &= \frac{1}{(mm')^{\frac{1}{2}}} \{-m' (k_\beta + k'_{\beta\beta}) + m (k_{\beta'} + k'_{\beta'\beta'}) + 2(m - m') k_{\beta\beta'}\} \\
 K_{67} &= \frac{1}{(mm')^{\frac{1}{2}}} \{m' (k_r - k'_{rr}) - m (k_{\alpha'} - k'_{\alpha'\alpha'})\} \\
 K_{89} &= \frac{1}{(mm')^{\frac{1}{2}}} \{m (k_{r'} - k'_{r'r'}) - m' (k_\alpha - k'_{\alpha\alpha})\}
 \end{aligned}$$

The expressions (7) when substituted into (5) give the frequencies in terms of the generalised valence force potential constants.

By making the substitution $m' = m$, $k_{r'} = k_r$, etc., these expressions reduce to those of Part I.

DISCUSSION OF THE RESULTS.

It is of interest to compare the frequencies of the AB_2C_2 (trans) molecule with those of the AB_4 and AC_4 molecules. This will be done to a valence force approximation. For AB_2C_2 (trans) the frequencies are given by

$$\begin{aligned}
 \lambda_1 &= \frac{k_r}{m}, \quad \lambda_2 = \frac{k_{r'}}{m'} \\
 \lambda_3 &= \frac{(a'm')^2 k_\alpha + (am)^2 k_{\alpha'}}{mm'(ma^2 + m'a'^2)}
 \end{aligned}$$

$$\begin{aligned}
 \lambda_4 + \lambda_5 &= \left(1 + \frac{2m}{M}\right) \frac{k\beta}{m} + \left(1 + \frac{2m'}{M}\right) \frac{k\beta'}{m'} \\
 \lambda_4 \lambda_5 &= \left(1 + \frac{2m}{M} + \frac{2m'}{M}\right) \frac{k\beta k\beta'}{mm'} \dots\dots\dots (8) \\
 \lambda_6 + \lambda_7 &= \left(1 + \frac{2m}{M}\right) \frac{k_r}{m} + \left(1 + \frac{2m'}{M}\right) \frac{k_\alpha'}{m'} \\
 \lambda_6 \lambda_7 &= \left(1 + \frac{2m}{M} + \frac{2m'}{M}\right) \frac{k_r k_\alpha'}{mm'} \\
 \lambda_8 + \lambda_9 &= \left(1 + \frac{2m'}{M}\right) \frac{k_r'}{m'} + \left(1 + \frac{2m}{M}\right) \frac{k_\alpha}{m} \\
 \lambda_8 \lambda_9 &= \left(1 + \frac{2m}{M} + \frac{2m'}{M}\right) \frac{k_r' k_\alpha}{mm'}
 \end{aligned}$$

where $\lambda_1 = 4\pi^2 c^2 v_1^2$.

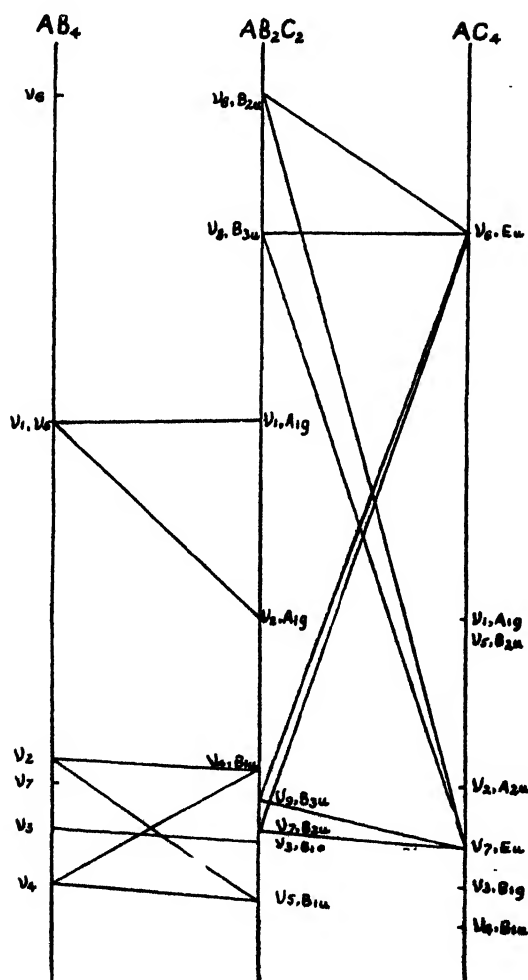


Fig. 3.—The correlation of the frequencies of the series AB_4 - AB_2C_2 - AC_4 . On the left-hand side is shown the correlation of the non-degenerate frequencies and on the right-hand side that of the degenerate frequencies.

If $m=m'$, $k_r=k_r'$, $k_\alpha=k_\alpha'$ and $k_\beta=k_\beta'$, these relations reduce to the valence force frequencies of the AB_4 molecule given by Wilson (1935).

If reasonable values are assumed for the constants occurring in the expressions (8), the frequencies of the three molecules AB_4 , AB_2C_2 (trans) and AC_4 can be determined. This is done in Fig. 3.

In the Raman spectrum of AB_4 two lines appear, while there are three in the infra red. For AB_2C_2 (trans), however, three lines appear in the Raman spectrum and six in the infra red. In either case, to determine the "out of the plane" force constants requires an investigation of the infra red spectrum.

SUMMARY.

Analytical expressions have been obtained for the normal co-ordinates of the planar AB_2C_2 (trans) molecule, together with the relationship between the constants of the general potential function and those of a valence force function, modified by the introduction of cross terms. A diagrammatic representation of the correlation between the frequencies of the series $AB_4-AB_2C_2$ (trans)- AC_4 to the valence force approximation is given.

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ERRATUM.

In Part I (*THIS JOURNAL*, **77**, 136) the right hand sides of the fourth and fifth equations of (21) should be interchanged.

SOME INTERFERENCE EFFECTS WITH MICA.

By O. U. VONWILLER, F.Inst.P.

With Plate XV.

Manuscript received, November 14, 1944. Read (in title only), December 6, 1944.

When white light is incident on a thin sheet of transparent material the spectrum of the transmitted light consists of a number of bright bands, the wave-lengths of maximum intensity being given by λ in the equation

$$2t\sqrt{n^2 - \sin^2 i} = p\lambda \dots\dots\dots (1)$$

where p is an integer, t the thickness of the sheet, n the index of refraction and i the angle of incidence. As is well known, the sharpness of the bands increases with the coefficient of reflexion and therefore is greatest for grazing incidence. The spectrum of the reflected light gives the complementary effect; at grazing incidence we have a continuous spectrum broken by sharp dark bands in the positions occupied by the bright bands in transmission.

Several years ago photographs showing these effects were prepared for class demonstrations; on these some observations were made that appear of sufficient interest to be put on record.

In Plate XV, (1) is the transmission spectrum through a thin sheet of mica, at large angle of incidence (about 88°). Two sets of bands are present as the material is doubly refracting, and from the band spacing it is seen that the dispersion differs for the two. One set of bands is distinctly sharper than the other, indicating a difference in the coefficient of reflexion.

All the spectra shown were obtained with the mica placed so that the directions of vibration were respectively in the plane of incidence and at right angles to it. The incident light was plane polarised, the relative intensities of the two systems of bands being controlled by altering the plane of polarisation. Spectrum (2) was obtained by turning the polariser so that one set of bands, the less sharp in (1), was completely suppressed. Numbers (3) and (4) are reflexion spectra corresponding with (1) and (2).

Numbers (9) to (14) are also transmission spectra, obtained with a different spectrograph. In (9), (10) and (11) the thickness was about 0.04 mm.; (9) shows the double refraction, in (10), the polariser was placed so as to cut out one of the rays; in both of these the light was at grazing incidence; in (11) the light was incident normally; the bands are much less sharp corresponding with the smaller coefficient of reflexion. In (12) and (13) we have spectra corresponding with (9) and (10) but for a much thinner sheet, t being about 0.006 mm., and in (14) we have a spectrum corresponding with (10), for a very thin sheet, t being only about 0.003 mm. Elsewhere it is shown how from observations on the bands the value of p for any band, the thickness of the mica, and the three principal indices of refraction for various wave-lengths can be determined.¹

¹ O. U. Vonwiller and F. L. Arnot. "Interference Phenomena with Thin Films," *Proc. Third Pan Pacific Science Congress, Tokyo, 1926*, Vol. II, pp. 1314-1322.

COMPARISON OF THICKNESS OF SHEETS OF MICA.

In (5) we have a transmission spectrum for a piece of mica that had been torn in two in such a way that different thicknesses were traversed by different portions of the light. Corresponding with these we see several distinct sets of bands. The sharpness of some of the bands suggested that observations on them might provide an accurate means of comparing the thicknesses of the corresponding portions of the mica.

The positions of the bands of each of three systems were read by means of a travelling microscope; in the case of the sharpest set it was found that the error of the mean was not more than one or two-thousandths of a millimetre; the means for the others were less accurate. The mean readings for the three sets, measured from an arbitrary zero, are given in Table 1; the number in brackets after each reading is the estimated error of the mean, in thousandths of a millimetre. The value of p , determined as described below, is given for each band.

TABLE 1.

p	Series 1.		p'	Series 2.		p''	Series 3.	
		Reading.			Reading.			Reading.
30	..	10.828 (1)	18	..	10.553 (5)	17		
31	..	12.167 (1)	19	..	12.807 (3)	18	..	11.937 (5)
32	..	13.575 (1)	20	..	15.208 (7)	19	..	14.351 (5)
33	..	15.037 (2)	21	..	17.781 (3)	20	..	16.973 (6)
34	..	16.551 (2)	22	..	20.513 (14)	21	..	19.782 (2)
35	..	18.139 (2)	23	..	23.442 (5)	22	..	22.719 (3)
36	..	19.782 (2)	24	..	26.573 (2)	23	..	25.904 (5)
37	..	21.502 (1)	25	..	29.914 (4)	24	..	29.339 (9)
38	..	23.285 (2)	26	..	33.535	25	..	33.012 (4)
39	..	25.147 (2)				26	..	36.976 (7)
40	..	27.084 (2)						
41	..	29.101 (1)						
42	..	31.209 (2)						
43	..	33.398 (2)						
44	..	35.690 (2)						
45	..	38.084						

If band p' of system 2 comes between bands p and $p+1$ of system 1 band, p' corresponds with $p+x$, where x is less than unity; by the application of methods described later, x may be determined to a high degree of accuracy.

If t and t' are the thicknesses of the two sheets of mica we have $\frac{t'}{t} = \frac{p'}{p+x}$ from equation (1), so that if p and p' are known and x determined we obtain the ratio of the thicknesses.

The value of p for a particular band can be found as follows: Let λ_1 and λ_2 be the wave-lengths of bands p and $p+q$ where q is known by counting from p . The wave-lengths can be determined by the usual method of a comparison line spectrum. If the index of refraction were constant we should have

$$p\lambda_1 = (p+q)\lambda_2$$

$$\text{and } p = \frac{q\lambda_2}{\lambda_1 - \lambda_2} \dots\dots\dots (2)$$

The index of refraction increases as the wave-length decreases so that the value of p , obtained from equation (2), is too great; with spectra such as those considered here, where p is relatively small, the excess is usually less than one and

neglecting it we have the value of p . Similarly p' is determined. Should a mistake be made in estimating p or p' it will be revealed by inconsistent values for the ratio of the thicknesses, obtained from readings with the different bands ; by trial the correct numbers are easily found.

The value of x was determined by one or other of the methods of inverse interpolation described in an article by K. Mader, in the *Handbuch der Physik*.² These are methods of successive approximation involving difference of the second, third and higher orders. In a table giving these differences for the lines of series one, apparently the most accurate of the three, it is found that the third order differences are fairly large, up to 0.020 mm., and that several are positive and several negative, the changes of sign alternating over part of the series, with the result that differences of the fourth order are also large, in some instances too large to be neglected, although the multiplying factor is generally very small. This is probably because the screw of the travelling microscope is faulty, instrumental errors being introduced in the readings considerably greater than the observational errors in series one, if not in the others. However the results given in Table 2 show that very good agreement is obtained from observations with the several bands of a series ; possibly that would be improved to some extent by the use of a better screw or by the application of calibration corrections, when the final limitation would be due to the observational errors, that is to the lack of sharpness of the bands. In those instances in which the value of x , the fractional part in column 2 or 5 of Table 2, was greater than 0.3, the value was determined by two modifications of the general formula given by Mader, and the result quoted is a mean value ; the differences were generally small, the largest being 0.0004.

TABLE 2.

p'	p	t/t'	p''	p	t/t''
19	31.45998	1.65579	18	30.83215	1.71290
20	33.11482	1.65574	19	32.53557	1.71240
21	34.77757	1.65610	20	34.27023	1.71351
22	36.43024	1.65592	21	36	
23	38.08603	1.65591	22	37.68674	1.71303
24	39.74109	1.65585	23	39.39540	1.71284
25	41.39070	1.65563	24	41.11510	1.71313
26	43.06109	1.65619	25	42.82685	1.71312
Mean	..	1.65589	Mean	..	1.71299

Table 2 gives the results obtained, comparing the bands of series 2 and 3 with those of series 1. Column 1 gives the values of p' , column 2 the corresponding values of p , and column 3 the ratio t/t' , obtained by dividing p by p' . In columns 4, 5 and 6 we have the corresponding results for the bands of series 3. The overlapping of band 36 of series 1 and band 21 of series 3 made precise position determination of band 21 impossible ; the corresponding ratios are omitted in Tables 2 and 3.

Before reference was made to the article mentioned a method of approximations was worked out that gave two values of x that might be, one slightly below, and the other slightly above, the correct value ; taking the mean of these, in effect, is applying a third order correction. Suppose the position of the band examined to be between bands p and $p+1$ of the comparison series ; let $f(p+x)$,

² *Handbuch der Physik*, Vol. 3, p. 615 et seq.

$f(p)$, etc., represent the readings of the various bands concerned; the two formulæ derived for x are

$$x = \frac{f(p+x) - f(p)}{f(p) - f(p-1) + \frac{f(p+x) - f(p-1)}{f(p+1) - f(p-1)} \times [f(p+1) - 2f(p) + f(p-1)]}$$

$$\text{and } 1-x = \frac{f(p+1) - f(p+x)}{f(p+1) - f(p) + \frac{f(p+x) - f(p)}{f(p+2) - f(p)} \times [f(p+2) - 2f(p+1) + f(p)]}$$

These formulæ were applied to a comparison of the bands of series 1 and 2 with those of series 3, the values of $f(p)$, $f(p+1)$, etc., being the readings of p'' in Table 1 and the values of $f(p+x)$ those of p or p' . The results are given in Table 3 where the values obtained from the two formulæ are indicated by the pairs of figures for the last two or three decimal places.

TABLE 3.

p'	p''	t''/t'	p	p''	t''/t
20	19.33522 346	0.96676 67	33	19.27030 6805	0.58392 88
21	20.29532 218	96644 29	34	19.84453 359	58366 63
22	21.25163 658	96598 621	35	20.42369 045	58353 44
23	22.23436 350	96671 67	36	21	
24	23.20090 19988	96670 66	37	21.59106 528	58354 66
25	24.16111 57	96644 46	38	22.18382 10	58378 76
26	25.13644 586	96679 75	39	22.77006 6900	58385 82
			40	23.35224 108	58381 78
			41	23.9332 28	58374 73
			42	24.5137 84	58366 77
			43	25.1008 10	58374 74
			44	25.6841 33	58373 71
Mean	..	0.96654	Mean	..	0.58372

The ratio of the two mean values given in Table 3 is 1.65583, in good agreement with the value of t/t' given in Table 2, 1.65589, while the reciprocal of the value of t''/t in Table 3 is 1.71315 as compared with 1.71299 for t/t'' in Table 2. Calculations by the above formulæ are made much more quickly than by the methods described in the *Handbuch der Physik*, and in a case such as this are at least as trustworthy.

These results, as well as an examination of the individual values leading to the means, indicate that the comparison of thickness can be made to an accuracy of the order of one in ten thousand. The thicknesses of the three portions of mica were about 0.0080, 0.0048 and 0.0047 mm. respectively, so that the error

in the value for the ratio of thicknesses corresponds with but a few Angstroms, that is less than the grating space for mica, about 9A.

REFLEXION AT MICA-ANTIMONY SURFACE.

On half of one side of a thin piece of mica a layer of antimony was deposited by an evaporation process. Light incident at grazing angle ($i=88^\circ$) on the uncoated side was reflected, and the reflexion spectra (6), (7), (8) were obtained. In these the upper half corresponds with the uncoated half of the mica, and the lower half with the antimony-coated portion.

In the upper part of (6) we see the usual two systems of bands, but apparently only one system in the lower half. In (7) and (8) the polariser was rotated so as to suppress each of the beams in turn. In (7) the change of phase at reflexion results in a considerable displacement of the band, while in (8) the displacement is much less, so that in (6) the two bands in the lower half are nearly coincident.

The phase change could be measured with considerable accuracy by applying the methods described earlier for the determination of the band displacement, though for other than grazing incidence there would be a lack of sharpness with corresponding decrease in accuracy. It was intended to explore this field further, as it might provide a useful method in the investigation of the optical properties of metals. Demands arising from war conditions made this impossible, but it is hoped that opportunity for further work in this field may be obtained in the future.

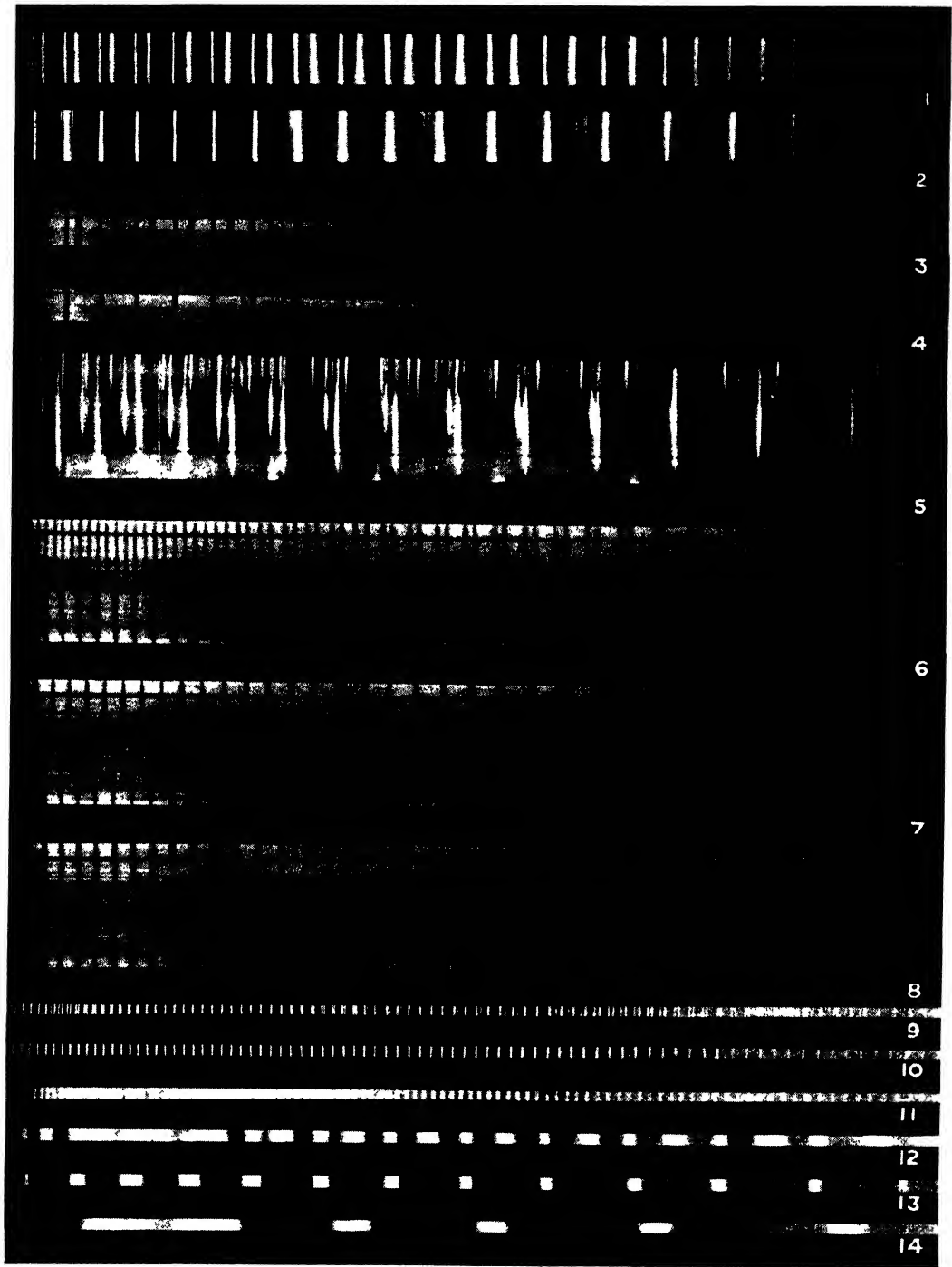
Spectra (9) to (14) on the plate were portion of a plate prepared for the paper by O. U. Vonwiller and F. L. Arnot at the Pan-Pacific Science Congress; it was not included in the volume probably because detail in some of the other spectra on the plate was too fine for reproduction.

I am indebted to Miss D. Tarrant, Commonwealth Research Assistant, and Mr. E. Warner for the preparation of an enlarged print, for the plate, of spectra selected from a number of original plates.

SUMMARY.

Measurements of the wave-lengths of the sharp bright bands in the spectrum of white light transmitted, at grazing incidence, through thin sheets of mica, ranging in thickness from $4\ \mu$ to $8\ \mu$, and the application of suitable interpolation formulæ, enable the ratio of the thicknesses to be determined with an accuracy of one in 10,000.

The fine dark lines in the spectrum of white light reflected at grazing incidence from a thin sheet of mica, half the back surface of which is coated with a metal, occupy different positions for the two halves, enabling the phase change at reflexion at the metal surface to be determined with considerable accuracy, suggesting a method for investigating optical properties of metals.



EXPLANATION OF PLATE.

- (1) Transmission spectrum, showing double refraction.
 - (2) Transmission spectrum, one set bands suppressed.
 - (3) Reflexion spectrum corresponding with (1).
 - (4) Reflexion spectrum corresponding with (2).
 - (5) Transmission spectrum, mica of irregular thickness.
 - (6) to (8) Reflexion spectra ; lower half of back surface coated with antimony.
 - (6) showing double refraction.
 - (7) electric vector in plane of incidence.
 - (8) electric vector perpendicular to plane of incidence.
 - (9) Transmission spectrum, showing double refraction.
 - (10) Transmission spectrum, one beam suppressed.
 - (11) Transmission spectrum, as (10) but for normal incidence.
 - (12) and (13) Transmission spectrum, corresponding with (9) and (10).
 - (14) Transmission spectrum, corresponding with (10) and (13).
- In all except (11) the angle of incidence was about 88° .

The approximate thicknesses were :

- 1 to 4 : 7.2μ .
- 6 to 8 : 12.0μ .
- 9 to 11 : 38.0μ .
- 12 and 13 : 5.8μ .
- 14 : 3.0μ .

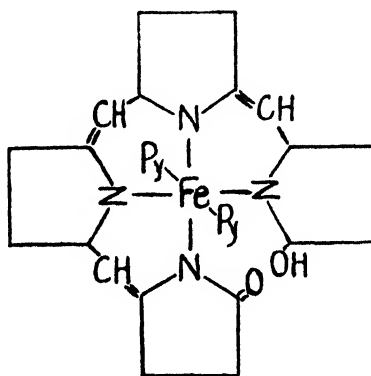
Magnification, Nos. 1-8, $\times 2.4$; Nos. 9-14, $\times 2.3$.

A NOTE ON THE MAGNETIC BEHAVIOUR OF VERDOHÆMOCHROMOGEN.

By D. P. CRAIG, M.Sc.,
and D. P. MELLOR, M.Sc.

Manuscript received, November 2, 1944. Read (in title only), December 6, 1944.

One of the oxidation products of hæmin is a green pigment to which the name verdohæmochromogen has been given. It has been assigned the following structure by Lemberg (1935, 1938):



This structure implies that (a) the porphyrin retains its general ring-like configuration after fission, and (b) the iron is ferrous and octahedrally linked to six nitrogen atoms. If the second statement is correct, then the molecule should be diamagnetic. Susceptibility measurements have been made on samples of verdohæmochromogen in order to determine whether iron in this compound is bivalent and whether it is ionically or covalently bound.

EXPERIMENTAL.

Measurements of susceptibility were made by the Gouy method on three different preparations.

Specimen 1 was an old specimen much of which was insoluble in chloroform. It proved to be paramagnetic with a moment of 4.0 Bohr magnetons (calculated on Lemberg's formula $\text{FeC}_{43}\text{H}_{43}\text{N}_6\text{O}_6$). The insolubility of this sample in pyridine indicated that it was largely an alteration product of verdohæmochromogen.

Specimen 2 was freshly prepared, but was handled without any precautions against oxidation. Its magnetic moment was 3.7 Bohr magnetons. Micro-analysis of the sample indicates the composition $\text{FeC}_{44}\text{H}_{55}\text{N}_6\text{O}_{14}$ instead of the expected $\text{FeC}_{43}\text{H}_{43}\text{N}_6\text{O}_6$. The magnetic moment was calculated using the analytical molecular weight.

Specimen 3 was freshly prepared and kept in an atmosphere of nitrogen until the time of measurement. Its moment was 2.16 Bohr magnetons. Analysis of this sample corresponds to the following formula, on the assumption that there is one atom of iron per molecule: $\text{FeC}_{43.3}\text{H}_{44.9}\text{N}_{5.8}\text{O}_{8.48}$.

DISCUSSION.

The fact that the most reliable sample measured did not correspond very closely to Lemberg's formula and the fact that verdohæmochromogen undergoes a change on standing, makes any interpretation of these results necessarily provisional. A small amount of diamagnetic material would not seriously affect the results, but the evidence is that the alteration products of verdohæmochromogen are paramagnetic.

On the assumption that specimen 3 contained but little alteration product, its magnetic behaviour is consistent with the view that the iron is in the covalent ferric condition as $K_3Fe(CN)_6$ ($\mu=2.33$ Bohr magnetons). This view about the valency of iron in verdohæmochromogen is held by other workers on chemical grounds (Fischer and Libowitzky, 1938; Libowitzky, 1940; Stier, 1942).

Because of some uncertainty regarding the purity of even the best specimen of the compound (3), it is perhaps safest to conclude that, whatever the valency of the iron in verdohæmochromogen, the iron is bound to the remainder of the molecule by covalent bonds.

ACKNOWLEDGEMENT.

We are indebted to Dr. R. Lemberg, who very kindly prepared the specimens of verdohæmochromogen used in this work.

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THE CHEMISTRY OF BIVALENT AND TRIVALENT IRIDIUM.

PART II. THE STANDARD OXIDATION REDUCTION POTENTIAL FOR THE CHLORIRIDITE-CHLORIRIDATE SYSTEM IN HYDROCHLORIC ACID SOLUTION.

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Manuscript received, November 8, 1944. Read, December 6, 1944.

It has been pointed out by Kolthoff and Tomsicek (1935) that many accepted values for standard oxidation reduction potentials are in error by as much as 0.1 volt because measurements were not carried out at sufficiently low ionic strengths. The oxidation reduction potential for the equilibrium between trivalent and quadrivalent iridium has been studied by Ogawa (1929) and more recently by Sho-Chow Woo (1931). Inconsistencies in the results of Ogawa (*loc. cit.*) lead Sho-Chow Woo (*loc. cit.*) to determine the potential for the system $\text{IrCl}_6^{3-} \rightleftharpoons \text{IrCl}_6^{4-}$ in 1 Normal hydrochloric acid, but no attempt was made to obtain the true standard oxidation reduction potential at infinite dilution (zero ionic strength). In this paper measurements are described in which the potential has been determined in hydrochloric acid of decreasing concentration down to that point where hydrolysis of the complex ion becomes serious.

The usual method of mixing analysed solutions of ammonium hexachloriridite and ammonium hexachloriridate with various amounts of hydrochloric acid was adopted, the solution being stirred in contact with an inert electrode until equilibrium was attained. Rhodium plated on glass was found to be the most satisfactory electrode, stable equilibrium being reached rapidly. Much trouble was experienced with other electrodes such as platinum or iridium plated platinum, a difficulty also encountered by Sho-Chow Woo (*loc. cit.*).

The system $\text{IrCl}_6^{3-} \rightleftharpoons \text{IrCl}_6^{4-}$ is of particular interest in that the oxidation-reduction potential diminishes with decreasing ionic strength instead of rising as with cationic systems such as ferrous-ferric iron. A similar case is the ferro-cyanide-ferricyanide system investigated by Kolthoff and Tomsicek (*loc. cit.*). This behaviour is in accord with the Debye-Huckel theory, the following calculation showing that for very low ionic strengths the oxidation-reduction potential, E , should be a linear function of \sqrt{I} .

For any reversible oxidation-reduction system

$$E = E_0 + \frac{RT}{nF} \ln \frac{a_{\text{Ox}}}{a_{\text{Red}}}$$

For the system $\text{IrCl}_6^{3-} \rightleftharpoons \text{IrCl}_6^{2-} + e^-$

$$\begin{aligned} E &= E_0 + \frac{RT}{F} \ln \frac{a_{\text{IrCl}_6^{2-}}}{a_{\text{IrCl}_6^{3-}}}, \quad (n=1) \\ &= E_0 + \frac{RT}{F} \ln \frac{C_{\text{IrCl}_6^{2-}} \times f_{\text{IrCl}_6^{2-}}}{C_{\text{IrCl}_6^{3-}} \times f_{\text{IrCl}_6^{3-}}} \\ &= E_0 + \frac{RT}{F} \ln \frac{C_{\text{IrCl}_6^{2-}}}{C_{\text{IrCl}_6^{3-}}} + \frac{RT}{F} \ln \frac{f_{\text{IrCl}_6^{2-}}}{f_{\text{IrCl}_6^{3-}}} \\ &= E_0 + \frac{RT}{F} \{ \ln f_{\text{IrCl}_6^{2-}} - \ln f_{\text{IrCl}_6^{3-}} \}, \quad \text{when } C_{\text{Ox}} = C_{\text{Red}} \\ &= E_0 + \frac{RT}{F} \{ -0.5 \times 2^2 \times \sqrt{I} + 0.5 \times 3^2 \times \sqrt{I} \} \times 2.303 \\ &= E_0 + \frac{RT}{F} \times 2.5 \sqrt{I} \times 2.303 \quad \text{at } 20^\circ \text{ C.} \\ &= E_0 + 0.145 \sqrt{I} \quad \text{at } 20^\circ \text{ C.} \end{aligned}$$

E = Oxidation-reduction potential at ionic strength I .

E_0 = Standard oxidation-reduction potential (zero ionic strength).

I = Ionic strength = $\frac{1}{2} \sum Z^2 c$.

Z = Valency of ion, $n = Z_{\text{Ox}} - Z_{\text{Red}}$.

C = Molar concentration for a given ion.

R = Universal gas constant.

F = Faraday's number.

f = Molar activity coefficient.

a_{Ox} = Activity of oxidant.

a_{Red} = Activity of reductant.

From the above calculation it is clear that under ideal conditions the oxidation-reduction potential of the system should decrease by 14.5 millivolts for every 0.1 unit decrease in $\sqrt{\text{ionic strength}}$. This limiting Debye-Huckel law holds only below an ionic strength of approximately 0.1. In the absence of much hydrochloric acid, at low ionic strengths, hydrolysis of the hexachloriridate ion becomes serious and hence the experimental values obtained cannot be expected to give a true value of E for the reversible system $\text{IrCl}_6^{3-} \rightleftharpoons \text{IrCl}_6^{2-} + e^-$. Since the standard oxidation-reduction potential is in any case a limiting value at infinite dilution, it is necessary to extrapolate from experimental data to obtain it. Extrapolation through experimental points obtained at low ionic strengths is clearly not satisfactory since hydrolysis of the complex ions makes it probable that at this dilution we are no longer dealing with the reversible system $\text{IrCl}_6^{3-} \rightleftharpoons \text{IrCl}_6^{2-}$. Under the circumstances, it was decided to obtain the limiting value of E_0 by assuming that the Debye-Huckel limiting law holds below the point where $\sqrt{I} = 0.2$, i.e. where $I = 0.04$, the point A in Fig. 1. This is justifiable on theoretical grounds and also because a smooth curve is obtained which would not be the case if experimental points below A were used. It is of interest to note that the experimental points below A all lie to the right of the Debye-Huckel slope. This is to be expected since hydrolysis would tend to

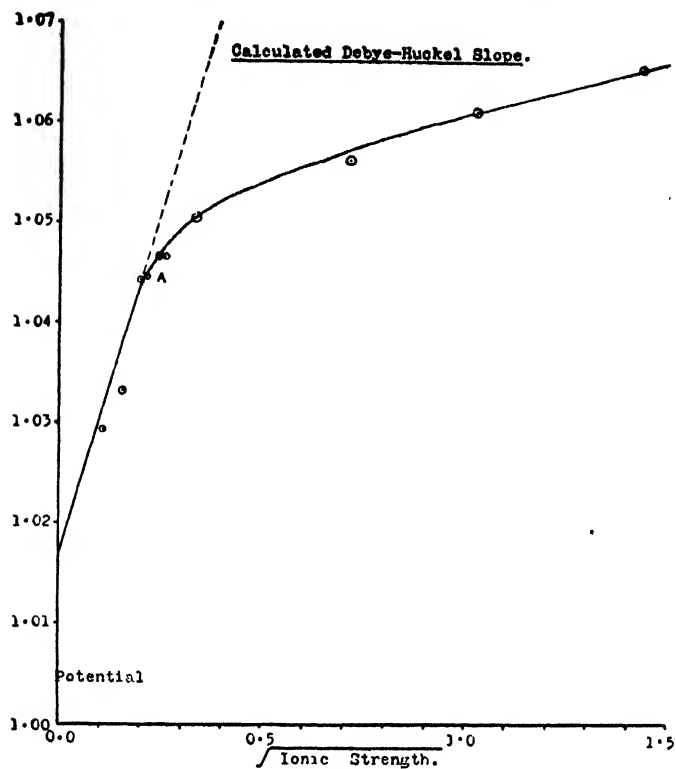


Fig. 1.

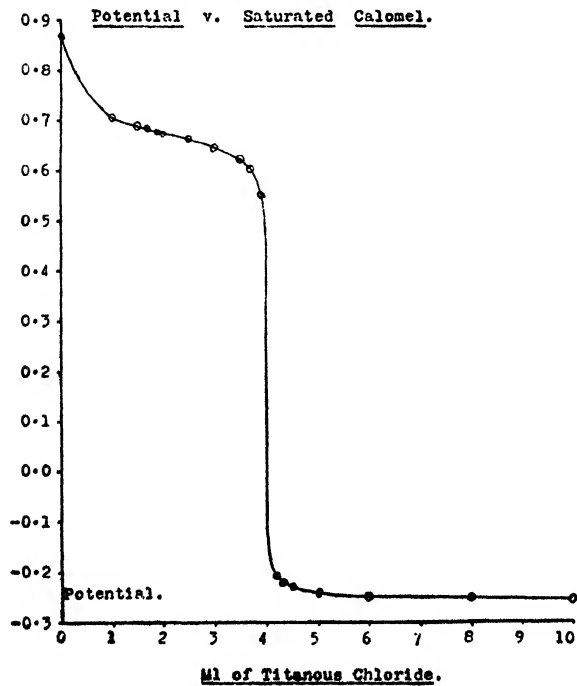
POTENTIOMETRIC TITRATION OF 10 ml(NH₄)₂IrCl₆ with H₂TiCl₆.Potential v. Saturated Calomel.

Fig. 2.

lower the activity of the oxidant more than the reductant and hence give a lower value for E . In the determination of E_0 for the stannous-stannic system by Huey and Tartar (1935) it was found that, for small values of I , the curve fell very steeply as I decreased. This behaviour was attributed to the greater hydrolysis of the stannic ion decreasing its activity more rapidly than that of the stannous ion.

From the graph (Fig. 1) it may be seen that the standard oxidation-reduction potential for the system $\text{IrCl}_6^{3-} \rightleftharpoons \text{IrCl}_6^{2-} + e^-$ is 1.017 volts at 20° C. on the standard hydrogen activity scale. The value for E_0 obtained by Sho-Chow Woo (*loc. cit.*) in 1 Normal hydrochloric acid was 1.021 volts; this result is lower than that obtained by the authors in this paper for that particular acid concentration. Two factors are suggested in explanation of the low result obtained by Sho-Chow Woo (*loc. cit.*)—the use of an iridium electrode, which the present authors have found is more readily attacked by chlorine and chloriridate ion than rhodium, and hence decrease the concentration of the oxidant at the electrode surface; and the failure to take the precaution of chlorinating the iridate solution so that the concentration of the oxidant ion had not been reduced by traces of impurity during the preparation of the solution.

EXPERIMENTAL.

Preparation of Solutions.

Ammonium Hexachloriridate. A warm concentrated solution of sodium hexachloriridate, made by heating iridium and sodium chloride in a current of chlorine, dissolving in water and filtering off the residue of undissolved iridium, was treated with excess ammonium chloride and allowed to crystallise overnight. The precipitated ammonium hexachloriridate was filtered through sintered glass, washed with hydrochloric acid at -10°C . and finally with ice cold water and dried at room temperature. 0.5 g. was dissolved in 100 ml. water (0.0113 molar), made approximately 0.063N with respect to hydrochloric acid, and divided into two parts. One part was treated with chlorine to oxidise any chloriridite which might be present and the excess chlorine removed with a current of air purified by passage through alkaline permanganate, acid permanganate and finally distilled water. The solution was then made up to the original volume with distilled water.

Ammonium Hexachloriridite. The second half of the above solution was refluxed with A.R. silver wire until reduction to trivalent iridium was complete, and the excess silver and silver chloride removed by filtration. Contrary to the impression gained from Sho-Chow Woo (*loc. cit.*), a small loss of iridium occurred during reduction, partly as insoluble silver hexachloriridite and partly as iridium metal. This was confirmed by dissolving the silver chloride out with ammonia when the greenish silver hexachloriridite was left insoluble; the latter on treatment with potassium cyanide left a grey deposit of iridium. The loss of iridium amounted to about 8%. The concentration of the chloriridite solution was determined by treating 5 ml. of the solution with an equal volume of hydrochloric acid then chlorinating and diluting to 100 ml.; the latter solution was then compared colorimetrically, using a Klett colorimeter, with 5 ml. of the chloriridate solution of known concentration treated similarly. The molecular ratio of chloriridate to chloriridite was found to be 1.083 : 1, for which a slight correction was necessary in the E.M.F. figures owing to the ratio of the concentrations of oxidant to reductant not being exactly 1 : 1.

Titanium Solution.

Approximately 10 g. pure redistilled titanium tetrachloride were dissolved in hydrochloric acid (5 normal) and reduced electrolytically with a lead cathode. The resultant solution was filtered and diluted with boiled out, distilled water and hydrochloric acid until the final concentration was 0.025 N with respect to titanous chloride and 1.113 N with respect to hydrochloric acid. Because of ease of aerial oxidation the titanous chloride solution was stored under carbon dioxide.

APPARATUS.

E.M.F. measurements were carried out by the usual Poggendorff compensation method using a Leeds and Northrup potentiometer capable of an accuracy of 0.1 millivolt. The galvanometer was a Cambridge moving coil type with lamp and scale, sensitive to 10^{-8} amp. A Weston standard cell was used.

The electrode vessel consisted of a 250 ml. pyrex, round bottom, five neck flask. The various openings allowed the ingress of the salt bridge, rhodium electrode, stirrer, burette and carbon dioxide when required. A semi-micro burette graduated to 0.05 ml. was used.

Electrodes.

Drawn out, sealed pyrex tubes were thoroughly cleaned in chromic acid and dipped in a 4% solution of rhodium trichloride deep enough to cover a fine platinum wire wound around the top of the tube to make contact. After drying, the rhodium trichloride was ignited, leaving a fine silvery deposit of rhodium. This was repeated three times and the rhodium plate washed with hot *aqua regia* and water many times and the platinum contact covered with Apiezon wax. The resistance of the electrode was about 50 ohms for three inches length.

The reference electrode consisted of a saturated calomel electrode connected through a saturated potassium chloride, agar-agar bridge to the electrode vessel. The potential of the calomel electrode was taken as 0.2476 volt at 20° C. as recommended by Dole (1940).

Other electrodes tried included pure platinum, rhodium-plated platinum and iridium-plated platinum. The deviations between the E.M.F. obtained whilst stationary and whilst stirring were initially of a much higher order than those obtained with the electrode finally adopted. Moreover, true equilibrium could not be reached with these electrodes irrespective of the time of stirring.

Titration of ammonium hexachloriridate with titanous chloride were carried out in carbon dioxide following an early suggestion that the oxidation-reduction potential might be obtained by this method by measuring E at 50% reduction. Owing to slowness in attaining equilibrium, results were too low. Potential mediators such as ceric sulphate and potassium iodide also failed to bring about equilibrium. Figure III shows the curve obtained in a typical titration. It will be observed that the fall in potential during the addition of the first 25% of reducing agent is much greater than might be expected. This is no doubt due to a false equilibrium being reached. It is of interest to note that the values for E obtained by this method also diminished with decreasing ionic strength, a curve of the same shape as Fig. I being obtained but all values were approximately 0.1 volt lower.

Experimental Procedure.

Equal volumes (5 ml.) of the hexachloriridite and hexachloriridate together with the appropriate amount of hydrochloric acid were made up to 30 ml. with distilled water. The mixture was stirred in contact with the electrode for many hours, a stable potential being reached after approximately one hour; this potential remained constant for periods up to two days. Initial potentials were approximately 15 millivolts too high and before equilibrium was reached there was a considerable difference between the potential when at rest and when stirring. However when equilibrium was established there was only a very small difference of the order of 0.2 to 0.3 millivolt. Although thermodynamic theory does not take into account a mechanical movement of the liquid relative to the electrode, which may interfere with the establishment of the electrical double layer, without thorough mixing there is no guarantee of definite equilibrium throughout the whole system, and in particular in the surface layer adjacent to the electrode. The effect of stirring is, however, seen to be negligible.

Over protracted periods the salt bridge was removed to prevent reduction, although tests showed this to be negligible. Stirring with carbon dioxide was found to give no detectable difference to that shown by mechanical stirring. Experimental results are shown in Table I, whilst the relation between \sqrt{I} and E is shown on the graph (Fig. I).

TABLE I.
Table of Results.

HCl Normality.	\sqrt{I} HCl.	\sqrt{I} Total.	E.M.F. (Corrected).
2.037	1.428	1.433	1.065 ⁶
1.029	1.014	1.023	1.061 ²
0.4890	0.699	0.711	1.056 ²
0.092	0.303	0.330	1.050 ⁵
0.0494	0.222	0.257	1.046 ⁶
0.0423	0.206	0.244	1.046 ⁷
0.0281	0.167	0.212	1.044 ⁷
0.0210	0.145	0.195	1.044 ³
0.0126	0.112	0.152	1.033 ¹
0.0063	0.079	0.107	1.029 ³

SUMMARY.

The standard oxidation-reduction potential for the hexachloriridite-hexachloriridate system has been determined by extrapolation from values obtained in hydrochloric acid of various concentrations. At 20° C. this has been found to be 1.017 volt.

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THE CHEMISTRY OF BIVALENT AND TRIVALENT RHODIUM.

PART VIII. RHODIC AND RHODOUS COMPLEXES WITH DIMETHYLGLYOXIME.

By F. P. DWYER, M.Sc.,
and R. S. NYHOLM, M.Sc.

Manuscript received, November 22, 1944. Read, December 6, 1944.

During the study of bivalent rhodium complexes, and in particular during the search for square complexes, the rhodic and rhodous compounds with dimethylglyoxime have been investigated. Rhodium in the bivalent state might be expected to react analogously to bivalent cobalt with this grouping and yield tetravalent as well as hexavalent compounds, similar to the simple bis compound $\text{Co}(\text{DH})_2^*$ (Mellor and Craig, 1940) and the halide complexes $[\text{CoCl}_2(\text{DH}_2)]$ and $[\text{CoCl}_2(\text{CH}_2)_2]$ (Thilo, 1931).

The rhodic compounds $\text{M}[\text{Rh}(\text{NO}_2)_2(\text{DH})_2] \cdot 2\text{H}_2\text{O}$ have been described by Lebedenski and Federov (1938), whilst Malatesta and Turner (1942), during an investigation of the colour reaction between dimethylglyoxime, cobalt chloride and sodium polysulphide, prepared the analogous rhodium compound $\text{Na}[\text{Rh}(\text{DH})_2\text{S}_6]$. There appears to be no record, however, of the reaction between the simple rhodic halides and dimethylglyoxime.

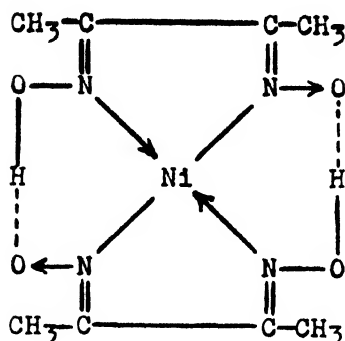
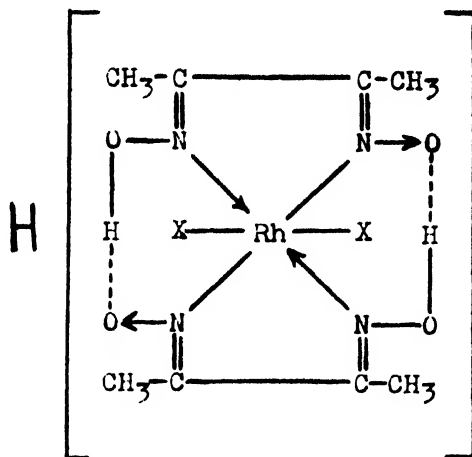
Solutions of the rhodic halides in varying acid concentrations from approximately five normal down to just sufficient acid to prevent hydrolysis, have been found to react with dimethylglyoxime to yield sparingly soluble bis-halide, bis-oxime complexes of the general formula $\text{H}[\text{RhX}_2(\text{DH})_2]$, which function as strong monobasic acids, giving stable, insoluble silver salts, and stable, water-soluble alkali metal, barium and ammonium salts. Treatment of these compounds with excess dimethylglyoxime and sodium acetate or caustic soda failed, even after many hours' boiling, to replace the halogen groups. The complex acids were soluble in ammonium oxalate, demonstrating their pronounced acidity, but many hours' refluxing failed to yield an oxalato compound, and the ammonium salt of the original acid crystallised out on evaporation. The halogen groups, thus, probably occupy trans positions in the octahedral complex—a conclusion reached by Lebedenski and Federov (*loc. cit.*). The halogen could not be precipitated by boiling with silver nitrate, which merely yielded the silver salt—itself easily soluble in dilute nitric acid. The halogen atoms are thus bonded covalently. Crystalline pyridine salts could be isolated, but they easily lost pyridine during drying.

From titration studies, and conductivity determinations on the chloride, which was the most soluble, it has been found that although three hydrogen atoms are present which might function as acidic, the substance acts exclusively as a monobasic acid, comparable in strength with hydrochloric acid. This observation has an interesting bearing on the structure of the well-known nickel dimethylglyoxime (I), which, although it has two hydrogen atoms that might be acidic, has been shown to fail in the reaction with phenylisocyanate (Tschugaeff, 1905) or with acetic anhydride (Barker, 1925) and yields no methane with methyl magnesium iodide (Brady and Muers, 1930). This lack of reactivity has been

* DH_2 = Dimethylglyoxime, $\text{H}_2 \cdot \text{C}_4\text{H}_8\text{N}_2\text{O}_2$.

suggested (Brady and Muers, *Ibid.*), as due to hydrogen bonding and a similar explanation seems feasible for the pronounced monobasic character of the rhodium compounds (II).

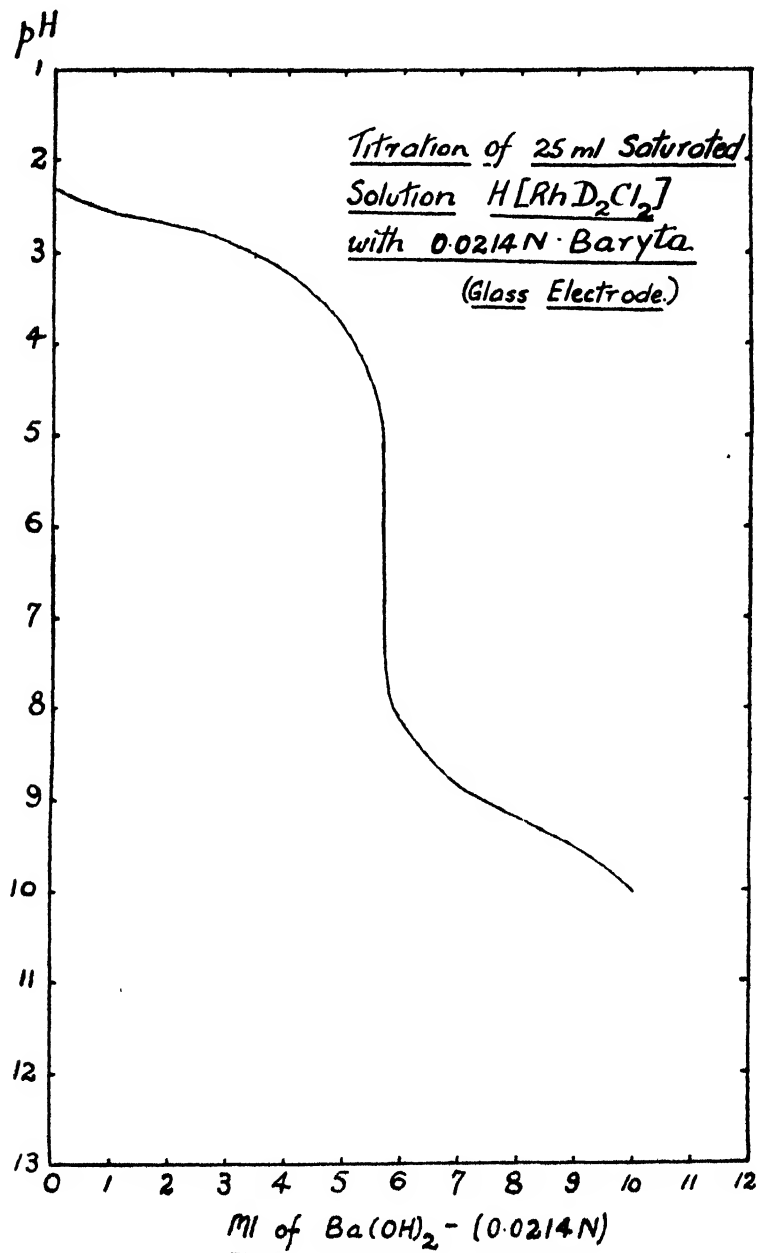
The rhodic compound $[\text{Rh}(\text{DH})_3]$ (III) was ultimately prepared in small yield from rhodic sulphate as a brown, highly insoluble powder. It was insoluble in alkalis, but dissolved in dilute hydrochloric acid to a reddish solution, containing probably the cis-dihalide-bis-glyoxime compound. The reddish solution lightened gradually and deposited the usual yellow trans compound (II).

III

The rhodic halide complexes on boiling with hypophosphorous acid in halogen acid solution gradually dissolved, but gave only a complex with hypophosphorous acid, the oxime apparently being destroyed by this reducing agent. In neutral or slightly acid solution in the presence of dimethylglyoxime, sodium formate, however, gave a black substance which very rapidly changed to the brown tris-glyoxime rhodic complex (III). This compound was soluble in caustic soda to a dark brown solution, which gave the original black substance on acidification, and reduced silver nitrate in the cold to the metal. Although, owing to oxidation, it was not possible to obtain specimens pure enough for analysis, it is probable that this is the tris-glyoxime rhodous compound $\text{H}[\text{Rh}(\text{DH})_3]$ (IV).

The black compound (IV) dissolved in warm dilute hydrochloric acid to an intense purplish-red solution, which very rapidly became lighter in colour due to oxidation. The purplish-red substance would appear to be the rhodous halide complex $\text{H}_2[\text{RhCl}_2(\text{DH})_2]$ (V), but all attempts at isolation failed. The reddish oxidised solution on evaporation at room temperature gave a mixture of red and yellow crystals. The yellow substance was readily identified as the usual rhodic halide complex (II), and the reddish crystals from tests applied under the microscope with individual crystals separated by hand were found to react strongly acid to litmus, were soluble in sodium acetate and caustic soda, and gave an orange-yellow silver salt. An aqueous solution on evaporation deposited yellow crystals of the usual complex (II). As the mode of preparation and reactions suggest the red compound is probably the cis complex $\text{H}[\text{RhCl}_2(\text{DH})_2]$ (VI).

In the structural formulation of compounds (III), (IV), (V), (VI), hydrogen bonding in the manner of (II) presents some difficulties since the chelate rings are skewed with respect to each other and sufficient distortion might then arise to prevent the formation of the relatively weak hydrogen bond. On the other hand if the normal hydroxyl oxime form is postulated, the tris-oxime complex (III), for instance, might reasonably be expected to be at least as acidic as the free oxime. Actually, it is quite insoluble in alkali. For this reason it is felt that some form of hydrogen bonding is present in these compounds.



Curve 1.

EXPERIMENTAL.

Monohydrogen dichloro-bisdimethylglyoxime rhodate^{III}. A slightly acid solution of rhodium trichloride (20 ml.), containing 0.19 g. rhodium was treated with dimethylglyoxime (0.8 g.), in alcohol (15 mls.), and refluxed for ten minutes. On cooling golden yellow rod-like crystals were precipitated. The crystals showed pronounced twinning, with characteristic V-shaped indentations at each end. A further yield was obtained by concentration of the mother liquor. The compound was washed with alcohol and finally ice water. On heating, the substance decomposed violently. It was slightly soluble in water, yielding an approximately 0.005 molar solution, which reacted strongly acid having a pH of 2.3. The compound was easily soluble in ammonia, caustic soda, sodium acetate and ammonium oxalate solutions, yielding salts, which regenerated the original substance by treatment with hydrochloric acid, but was only sparingly soluble in organic solvents.

For the conductimetric measurements, the pure silver salt was decomposed with the theoretical weight of sodium chloride by shaking at room temperature for ten hours, and the determinations made on the sodium salt so obtained. $\Lambda_{1024}=65.5$ and $\Lambda_{32}=56.7$. Hence difference=8.8. From the expression $\Lambda_{1024}-\Lambda_{32}=10 \times \text{basicity}$, the acid is monobasic.

The pH curve of the titration of a saturated solution of the substance with barium hydroxide using a glass electrode is shown in titration curve I, and shows the substance to be a strong monobasic acid.

Found: Rh=25.7%; Cl=17.4%. Calculated for $\text{H}[\text{RhCl}_2(\text{C}_2\text{N}_2\text{H}_7\text{O}_2)_2]$: Rh=25.4% Cl=17.53%.

Silver dichloro-bisdimethylglyoxime rhodate^{III}. The acid compound above (0.2 g.) was dissolved in sodium acetate solution, and treated in warm solution with a warm solution of silver nitrate (0.28 g.). The initially amorphous yellow precipitate rapidly crystallised on shaking and was filtered off and washed with warm water until the washings were free of silver ion. The compound was soluble in dilute nitric acid to a clear solution, and precipitated the halogen only on heating with an acid sufficiently concentrated to destroy the oxime group.

Found: Rh=20.3%; Cl=13.9%. Calculated for $\text{Ag}[\text{RhCl}_2(\text{C}_4\text{N}_2\text{H}_7\text{O}_2)_2]$: Rh=20.0%; Cl=13.87%.

Monohydrogen dibromo-bisdimethylglyoxime rhodate. This compound was prepared as for the chloro compound above, using rhodic bromide in hydrobromic acid solution. The bright yellow rod-like crystals were sparingly soluble in water to an acid solution, and gave an orange-silver salt.

Found: Rh=20.8%; Br=32.4%. Calculated for $\text{H}[\text{RhBr}_2(\text{C}_4\text{N}_2\text{H}_7\text{O}_2)_2]$: Rh=20.8%; Br=32.39%.

Monohydrogen di-iodo-bisdimethylglyoxime rhodate^{III}. Rhodium trichloride solution (20 mls.) was treated with potassium iodide (5 g.) and heated to 80° C. Dimethylglyoxime in alcohol as before was now added and the mixture refluxed until a brown crystalline precipitate appeared. The compound was very sparingly soluble in water, but the solution reacted acid, and gave a reddish brown silver salt. The silver salt on solution in nitric acid and warming gradually deposited silver iodide.

Found: Rh=17.58%. Calculated for $\text{H}[\text{RhI}_2(\text{C}_4\text{N}_2\text{H}_7\text{O}_2)_2]$: Rh=17.50%.

Tris-dimethylglyoxime rhodium^{III}. A weakly acid solution of rhodic sulphate (20 mls.) containing 0.19 g. rhodium was treated with dimethylglyoxime 0.6 g. in alcohol (15 ml.) and refluxed for some time. A solution of sodium acetate 3 N. (20 ml.) was then added and finally caustic soda, until the solution was very faintly alkaline. A dark brown precipitate gradually came down, and the solution was then made acid with acetic acid. The brown precipitate was filtered, and washed many times with alcohol. It was insoluble in all organic solvents, but dissolved in hydrochloric acid to a reddish solution, which gradually lightened and deposited yellow crystals of the chloro complex.

Found: Rh=22.9%. Calculated for $[\text{Rh}(\text{C}_4\text{N}_2\text{O}_2\text{H}_7)_3]$: Rh=22.9%.

Mono-hydrogen-tris-dimethylglyoxime rhodium^{II}. The chloro rhodic compound above (0.5 g.) was dissolved in aqueous sodium acetate (20 mls.), heated to boiling with dimethylglyoxime

(0.5 g.) in 15 mls. of alcohol, and a 20% solution of sodium formate added drop by drop until a black precipitate appeared. The solution was then rapidly cooled to prevent complete reduction to rhodium metal, and filtered. The black precipitate almost instantly commenced to become brown due to aerial oxidation. It proved impossible to dry the substance without oxidation occurring. The substance was soluble in caustic soda to a dark brown solution. A solution in alcohol, in which it was slightly soluble, instantly reduced silver nitrate to the metal, but even on complete decomposition with nitric acid no halogen could be found.

Mono-hydrogen-cis-dichloro-bis-dimethylglyoxime rhodate^{III}. The rhodous compound above was dissolved in warm hydrochloric acid 2 N., when it gave an intense purplish-red solution of (probably) the cis-dichloro rhodous compound, and rapidly commenced to lighten in colour. By shaking in air for a minute this oxidation was completed to a lighter reddish solution, which was then evaporated rapidly in a current of cold air. A mixture of yellow rods of the usual trans-dichloro compound and orange-red prisms was obtained. By recrystallisation much of the red compound was transformed to the yellow compound, but the reactions of the red substances were determined (*q.v. supra*) on individual crystals under the microscope. Even from a number of preparations, insufficient material was obtained for analysis.

SUMMARY.

Rhodic halides and dimethylglyoxime yield in addition to the tris-glyoxime complex, a series of strong, complex, dihalogen bis-glyoxime acids, in which the metal is always hexavalent. The rhodous compounds were also hexavalent, and oxidised very rapidly in the air.

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**CORRECTION OF PAPER "ON CONTACT TRANSFORMATIONS
ASSOCIATED WITH THE SYMPLECTIC GROUP".**

(THIS JOURNAL, Vol. LXXVI, 1942, 177-181)

By H. SCHWERDTFEGER.

It has been pointed out by M. S. Knebelman (*Math. Reviews* 4, 1943, 184) that the simple substitute for the lemma of Radon used in my proof of the theorem on the symplectic determinant ($\delta = +1$) is incorrect. Hitherto I have not been able to provide for Radon's original lemma (mentioned in footnote 5, *l.c.* 180) a purely algebraic proof such that it would be possible to save the simple formal structure of the proof of the above theorem which, indeed, was the main purpose of my paper.

While I still hope to find an algebraic proof of Radon's lemma, I have now reasons to believe that such a proof is not going to be simple. Therefore the proof of the theorem based upon the lemma will not excel by simplicity all the existing proofs for which references have been given in my paper.

ABSTRACT OF PROCEEDINGS
OF THE
Royal Society of New South Wales

April 5th, 1944.

The Annual Meeting, being the six hundred and twelfth General Monthly Meeting of the Society, was held in the Hall of Science House, Gloucester and Essex Streets, Sydney, at 7.45 p.m.

The President, Dr. A. B. Walkom, was in the chair. Forty-three members were present. The minutes of the previous meeting were read and confirmed.

The following were elected officers and members of the Council for the coming year :

President :

G. D. OSBORNE, D.Sc., Ph.D.

Vice-Presidents :

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A. BOLLIGER, Ph.D., A.A.C.I.

PROF. H. PRIESTLEY, M.D., Ch.M., B.Sc.
A. B. WALKOM, D.Sc.

Hon. Secretaries :

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D. P. MELLOR, M.Sc.

Hon. Treasurer :

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F. R. MORRISON, A.A.C.I., F.C.S.
R. S. NYHOLM, M.Sc.
H. H. THORNE, M.A., B.Sc., F.R.A.S.
H. W. WOOD, M.Sc., A.Inst.P., F.R.A.S.

The Annual Balance Sheet and Revenue Account were submitted to members by the Honorary Treasurer, and on the motion of Mr. A. Clunies Ross, seconded by Mr. A. E. Stephen, were adopted.

THE ROYAL SOCIETY OF NEW SOUTH WALES.

BALANCE SHEET AS AT 29th FEBRUARY, 1944.

LIABILITIES.

1943.			1944.		
£		£ s. d.	£	s.	d.
	Accrued Expense	35 0 0			
6	Subscriptions Paid in Advance	9 9 0			
				44	9 0
92	Life Members' Subscriptions—Amount Carried Forward			81	0 0
	Trust and Research Funds (detailed below)—				
1,799	Clarke Memorial	1,834 4 7			
690	Walter Burfitt Prize	725 15 0			
681	Liversidge Bequest	725 15 0			
	Research	3,049 5 0			
				6,334	19 7
28,284	Accumulated Funds (detailed below)			25,397	11 11
	Contingent Liability—In connection with perpetual				
	leases granted to the Australian National Research				
	Council and the Pharmaceutical Society of N.S.W.				
	Maximum liability, £901 16s. 8d.				
<u>£31,552</u>			<u>£31,858</u>	<u>0</u>	<u>6</u>

ASSETS.

1943.			1944.		
£		£ s. d.	£	s.	d.
470	Cash at Bank and in Hand			450	18 6
	Investments—Commonwealth Bonds and Inscribed				
	Stock—at Face Value—				
	Held for Clarke Memorial Fund	1,800 0 0			
	Held for Walter Burfitt Prize Fund	700 0 0			
	Held for Liversidge Bequest	700 0 0			
	Held for Research Fund	3,000 0 0			
	Held for General Purposes	3,160 0 0			
9,038				9,360	0 0
	Prepayment			28	12 0
	Debtors for Subscriptions	101 1 0			
	Deduct Reserve for Bad Debts	101 1 0			
14,756	Science House—one-third Capital Cost			14,756	0 0
6,800	Library (at Valuation)			6,800	0 0
436	Furniture (at Cost—less Depreciation)			414	0 0
38	Pictures			35	10 0
14	Lantern			13	0 0
<u>£31,552</u>			<u>£31,858</u>	<u>0</u>	<u>6</u>

TRUST AND RESEARCH FUNDS.

	Clarke Memorial.	Walter Burfitt Prize.	Liversidge Bequest.	Research.
	£ s. d.	£ s. d.	£ s. d.	£ s. d.
Balance at 28th February, 1943 ..	1,798 15 8	690 7 5	680 16 3	—
Transfer from Accumulated Funds	1 4 4	9 12 7	19 3 9	3,000 0 0
Capital at 29th February, 1944	£1,800 0 0	£700 0 0	£700 0 0	£3,000 0 0
Revenue—Interest on Investments..	65 10 2	25 15 0	25 15 0	99 5 0
Deduct Expenditure	31 5 7	—	—	50 0 0
Balance at 29th February, 1944 ..	£34 4 7	£25 15 0	£25 15 0	£49 5 0

ACCUMULATED FUNDS.

	£	s.	d.
Balance at 28th February, 1943	28,284	0	4
Deduct Transfer to other Funds	3,030	0	8
	£25,253	19	8
Add Adjustment of Investments	21	3	9
Reduction of Reserve for Bad Debts ..	9	9	0
Surplus for Year (see Income and Expenditure Account)	112	19	6
Balance at 29th February, 1944	£25,397	11	11

A. CLUNIES ROSS,
Hon. Treasurer.

The above Balance Sheet has been prepared from the books of account, accounts and vouchers of The Royal Society of New South Wales, and is a correct statement of the position of the Society's affairs on the 29th February, 1944, as disclosed thereby. We have obtained certificates showing that the whole of the Bonds and Inscribed Stock are held by the Society's Bankers for safe keeping.

HORLEY & HORLEY,
Chartered Accountants (Aust.).

Prudential Building,
39 Martin Place,
Sydney, 15th March, 1944.

INCOME AND EXPENDITURE ACCOUNT.

1st March, 1943, to 29th February, 1944.

1942-3.		1943-4.	
£		£ s. d.	£ s. d.
268	To Printing and Binding Journal—Vol. 76	412 1 7	
293	„ Salaries	302 12 0	
57	„ Library—Purchases and Binding	117 8 6	
50	„ Printing—General	72 17 11	
67	„ Miscellaneous	55 8 4	
58	„ Postage and Telegrams	53 14 11	
35	„ Rent—Science House Management Committee	43 3 8	
36	„ Cleaning	36 0 0	
26	„ Depreciation	25 0 0	
21	„ Telephone	17 11 11	
14	„ Insurance	14 12 2	
13	„ Audit	12 12 0	
7	„ Electricity	11 9 3	
	„ Repairs	5 10 0	
<hr/>			
945			1,180 2 3
481	„ Surplus for Twelve Months		112 19 6
<hr/>			
£1,426			£1,293 1 9
<hr/>			
1942-3.		1943-4.	
£	£	£ s. d.	£ s. d.
	485 By Membership Subscriptions		470 8 0
	400 „ Government Subsidy		400 0 0
	315 „ Science House—Share of Surplus		300 0 0
	196 „ Interest on General Investments		105 4 8
30	„ Receipts from Reprints	21 9 7	
32	„ Less Expenditure	17 6 0	
<hr/>			
—	—2		4 3 7
	9 „ Other Receipts		2 5 6
	23 „ Proportion of Life Members' Subscriptions		11 0 0
<hr/>			
£1,426			£1,293 1 9
<hr/>			

The Annual Report of the Council (1943-44) was read, and on the motion of Professor Elkin, seconded by Mr. E. Cheel, the report was adopted.

REPORT OF THE COUNCIL, 1943-1944 (RULE XXVI).

We regret to report the loss by death of three members since April 1st, 1943 : James Edward Mills (1940), John Job Crew Bradfield (1922) and Archibald Howie (1936) ; also of an honorary member, Frederick Chapman (1939).

By resignation the Society has lost five members : Mrs. Margaret Maccoll, Miss V. Suvoroff, Professor J. Macdonald Holmes, Alban J. M. Murray and Alan M. Willison.

The names of thirteen members have been removed from the register and their arrears have been written off.

The membership now stands at 287, eighteen new members having been elected during the year, namely William Kevin McCoy, William Dudgeon, Ronald Arthur Plowman, Leonard Winch, Jean Annie Kimble, Thomas Iredale, Ivan Stewart Turner, Reginald John Nelson Whiteman, Ernest Patrick Molloy, John William George Neuhaus, James Foote Walker, Mrs. Daphne Luber, Howard Hamlet Gordon McKern, John Kenneth Moore Simpson, Alexander Campbell Nicol, Barbara Joyce Burfitt and John Stanton Burkitt.

Eleven ordinary meetings of the Council were held during the year beginning 1st April, 1943, at which the average attendance was 14. During the same period nine general monthly meetings were held, with an average attendance of 35 members.

Eighteen papers were accepted for reading and publication during the year, and the following short talks were given :

“ Reflection of Light from Film-covered Glass ”, by Mr. J. Bannon, B.Sc.

“ Evaporated Metal Films ”, by Mr. F. P. J. Dwyer, B.Sc.

“ Biotin ”, by Professor H. Priestley, M.D., Ch.M., B.Sc.

“ Penicillin and Gramicidin ”, by Dr. F. Lions.

“ The Future of the Native Peoples of the South-west Pacific ”, by Professor A. P. Elkin.

An exhibit—"A New Source of Light—the Fluorescent Lamp"—was given by Mr. D. P. Mellor, M.Sc.

Popular Science Lectures.—On account of the lifting of lighting restrictions it was decided to revert to the holding of Popular Science Lectures during the winter months of 1943, and the following lectures were given:

"How We Came to Stand Upright", by Professor Harvey Sutton, O.B.E., M.D., Ch.B., D.P.H., B.Sc.

"Veterinary Science and the Community", by Mr. H. Parry, B.A.

"Exploring the Inside of the Earth", by Professor L. A. Cotton, M.A., D.Sc.

"Soviet Research on Applied Botany", by Professor Eric Ashby, D.Sc.

"Architecture: the Setting for Life", by Professor L. Wilkinson, F.R.I.B.A., F.R.A.I.A.

The attendances at most of the lectures were very good.

Clarke Memorial Lecture.—The Clarke Memorial Lecture for 1943 was given by Dr. H. G. Raggatt, Director of the Commonwealth Mineral Resources Survey, and was entitled "Australia's Mineral Industry in the Present War".

Clarke Memorial Medal for 1943.—The Medal was awarded to Dr. W. L. Waterhouse, in recognition of his contributions to plant pathology, in particular, his researches on rust in wheat.

The Royal Society's Medal was awarded to Mr. Edwin Cheel for his contributions to botanical science and for his work for the advancement of science in general. This was the first award of the Society's medal since 1896.

The Bi-centenary of the Birth of Sir Joseph Banks was commemorated at a general meeting of the Society, when a lecture on "Sir Joseph Banks and Australia" was given by Dr. G. Mackaness.

Commemoration of Other Events.—At the November monthly meeting the 400th anniversary of the publication of two important works was celebrated, namely "De Revolutionibus Orbium Coelestium", by Copernicus, and "De Humani Corporis Fabrica", by Vesalius. Lantern lectures were given by the Rev. Father D. J. O'Connell, on Copernicus, and by Dr. Leslie Cowlshaw, on Vesalius. Professor Shellshear, in proposing a vote of thanks to the lecturers, pointed out how Copernicus and Vesalius expressed in their works the urge for truth which was abroad in their period.

Centenary of the Foundation of the Royal Society of Tasmania.—The greetings of the Royal Society of New South Wales were sent to the Royal Society of Tasmania, which celebrated its centenary on October 12th, 13th and 14th, 1943. The occasion was marked by the striking of special medals, to be presented to the Royal Society of London, and the Royal Societies in each State of the Commonwealth, and to Professor Ashby and Dr. Mackaness, who had been invited to deliver lectures during the centenary celebrations.

Supply of Paper for Scientific Periodicals.—Attention having been drawn to a possible shortage of paper for the printing of scientific periodicals, it was resolved to write to the Chairman of the Book Publication Committee, pointing out the necessity for continuing the publication of research work, and asking that paper be made available for the purposes of the scientific journals.

A reply was received intimating that careful consideration was being given to technical and scientific publications, and that when possible to afford some relief to the scientific journals the Royal Society would be advised.

Government Grant.—A grant of £400 was received from the Government of New South Wales. The Government's continued interest in the Society's work is much appreciated.

Science House.—The Royal Society's share of the profits on Science House during the period from March 1st, 1943, to February 29th, 1944, has been £300.

Science House Management Committee.—The Royal Society has been represented at meetings of the Management Committee of Science House by Mr. A. R. Penfold and Dr. G. D. Osborne, with Mr. Alan Clunies Ross and Dr. F. Lions as substitute representatives. On the resignation of Dr. Lions, Mr. H. H. Thorne was appointed in his place.

Medals.—A gift was received from Mr. Henry F. Halloran, one of our senior members, for the purpose of providing two medals, one of which was to be awarded for distinguished services to science, and human welfare in the Southern Hemisphere. After consultation with the donor, it was decided to call this medal "The James Cook Medal", and the other one "The Edgeworth David Medal". A special committee has consulted with Mr. H. E. Dadswell concerning the designs, and finality will be reached in the near future.

With these two medals the Society will be responsible for the award of five medals: the other three are the Society's own medal (revived after a lapse of 48 years), the Clarke Memorial Medal and the medal which goes with the Walter Burfitt Prize.

The Council decided that the scope of these awards should be as follows :

The Edgeworth David Medal, donated by Mr. Henry Halloran, to encourage the younger research worker, is to be presented annually for distinguished contributions in one of the following fields, namely biological science, physical science, or social science, such fields of research to be considered in turn in successive years. Recipients shall be under thirty-five years of age, and the work done shall be in or on Australia and New Zealand.

The Clarke Memorial Medal may be awarded from time to time for distinguished work in natural science, done in or on the Australian Commonwealth or its territories; the person to whom the award is made may be resident in the Australian Commonwealth or its territories, or elsewhere. Natural science, for the purpose of the award, has been defined as geology, zoology and botany.

The Walter Burfitt Prize and Medal consists of a bronze medal and a money prize of £50, awarded at intervals of three years to the worker in pure and applied science resident in Australia or New Zealand whose papers or other contributions published during the past three years are deemed to be of the highest scientific merit, account being taken only of investigations described for the first time, and carried out mainly in these Dominions.

The Royal Society's Medal may be awarded at any time at the discretion of the Council to any member of the Society who has made meritorious contributions to the advancement of science in Australia.

The award will be considered annually, but not necessarily awarded annually.

The James Cook Medal, donated by Mr. Henry Halloran, is to be awarded not more than once annually for outstanding contributions to science and human welfare in and for the Southern Hemisphere.

For the purposes of this award, there shall be no limitations of the field of science or its applications, and Southern Hemisphere shall include South Africa, South America, Australia, New Zealand, all the Dutch East Indies and the islands of the southern seas.

Research Grants.—It was resolved to set aside a portion of the funds of the Royal Society of New South Wales to form the nucleus of a research fund, the income from which is to be made available to assist research workers.

Finance.—The audit of the Society's accounts shows that the finances are in a satisfactory condition. During 1943, £300 has been invested in war loans.

The Royal Society's Library.—*Librarian*.—Mr. W. H. Maze, who had done much good work for the library, tendered his resignation owing to pressure of other duties, and Mr. H. W. Wood was appointed in his place. Dr. A. Bolliger acted as assistant librarian.

Purchase of Periodicals and Binding.—The amount of £30 12s. 6d. has been expended on the purchase of periodicals, and the amount of £88 16s. has been spent on binding. The total amount expended on the library was thus £117 8s. 6d. Of this, £16 7s. 6d. was for binding done in 1942, so the total for 1943 is actually £101 1s.

Exchanges.—The number of volumes now being sent to other societies is 225.

Accessions.—For the twelve months ended in February, the number of accessions entered in the catalogue was 1,585 parts of periodicals and 136 whole volumes.

Borrowers and Readers.—Members and visitors reading in the library numbered thirty-seven.

The number of books and periodicals borrowed by members, institutions and accredited readers was seventy-one.

Among institutions which made use of the arrangements for inter-library borrowing were : The University of Sydney (Fisher Library and Botany School), the University of Western Australia, the C.S.I.R. Food Preservation Laboratory, the McMaster Laboratory, the Veterinary Research Station, Glenfield, the National Standards Laboratory, the National Herbarium of Melbourne, the Commonwealth Forestry Bureau, Canberra, the Sydney Technical College, Department of Public Works, Sydney, the Standards Association of Australia, the Colonial Sugar Refining Company, the Sydney County Council, and Amalgamated Wireless Research Laboratory.

Disposal of Old Books.—A number of out-of-date printed lists of members of several societies abroad, such as the Iron and Steel Institute, Institution of Mechanical Engineers, England, and the American Society of Civil Engineers, have been disposed of.

Text books on mathematics and astronomy were presented to the University of Sydney, the Sydney Observatory and Riverview Observatory.

Supplement to Pitt's Catalogue.—At the request of the Institute of Librarians, a list to date of periodicals received in the Royal Society's library was prepared and forwarded for reference in the Public Library. This action was suggested by the Institute of Librarians because, owing to wartime conditions, it has not been possible to issue a third supplement to Pitt's Catalogue.

It was resolved to make available to other libraries, on request from the Public Library, bound volumes containing specific articles. It was decided that unbound parts could be referred to in the Royal Society's library on a request being received from the Public Library.

Duplication in the Libraries of Science House.—The review of the list of periodical sets common to the libraries of the Royal Society of New South Wales and the Linnean Society of N.S.W. is now complete. It has been divided into three main categories, namely sets which should be retained by both libraries, sets which should be retained by the Linnean Society only, and sets which should be retained by the Royal Society only. The acceptance of such division would serve to relieve the congestion in the library very considerably. The matter has still to be considered by the Council.

The certificates of two candidates for admission as ordinary members of the Society were read for the first time.

Clarke Memorial Medal.—The announcement was made of the award of the Clarke Memorial Medal for 1944 to Professor W. E. Agar.

Election of Auditors.—On the motion of Professor Elkin, seconded by Mr. R. W. Challinor, Messrs. Horley and Horley were re-elected auditors of the Society for 1944-45.

Library.—The following donations were received: 350 parts of periodicals, 20 whole volumes.

The President, Dr. A. B. Walkom, delivered his address, entitled "The Succession of Carboniferous and Permian Floras in Australia".

Dr. A. B. Walkom then installed Dr. G. D. Osborne as President for the year 1944-45. Dr. Osborne thanked the members for the honour they had done him in electing him President. He then called upon Mr. C. A. Sussmilch to propose a vote of thanks to the retiring President for his interesting address, and for the work he had done for the Society during his presidential term. This was carried by acclamation.

The following papers were read by title only:

"Generalisation of Maxwell's Equations", by P. Foulkes. (Communicated by Prof. E. M. Wellish.)

"Some Lower Cretaceous Foraminifera from Bores in the Artesian Basin, Northern New South Wales", by Irene Crespin, B.A. (Communicated by Dr. Ida A. Brown.)

"A Note on the Role of the Nitrosyl Group in Metal Complexes", by D. P. Mellor and D. P. Craig.

May 3rd, 1944.

The six hundred and thirteenth General Monthly Meeting of the Royal Society of New South Wales was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. G. D. Osborne, was in the chair. Twenty-two members were present. The minutes of the previous meeting were read and confirmed.

The death was announced of the following member: Dr. Norman Dawson Royle, a member since 1929.

The certificates of four candidates for admission as ordinary members of the Society were read for the first time.

The certificates of two candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Alwynne Drysdale Bennett and Daniel George Moye.

Clarke Memorial Lecture.—It was announced that the Clarke Memorial Lecture for 1944 would be delivered at Science House on May 30th, at 8 p.m., by Dr. W. H. Bryan, M.C., the title being "An Australian Geologist Looks at the Pacific".

Library.—The following donations were received: 75 parts of periodicals and one whole volume.

Correspondence.—A letter calling attention to the agenda paper for the A.A.S.W. Conference on "The Planning of Science" was read.

The following papers were read:

"Geomorphology of the Central Eastern Area of New South Wales", by W. H. Maze, M.Sc.

Papers read by title at the April meeting were open for discussion.

Miss Irene Crespin, who was present as a guest, discussed her paper on "Some Lower Cretaceous Foraminifera from Bores in the Artesian Basin, Northern New South Wales".

Lecturette.—A lecturette on "Potential Topography in Electronics" was given by Dr. A. L. Reimann.

June 7th, 1944.

The six hundred and fourteenth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. G. D. Osborne, was in the chair. Thirty-two members and six visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of four candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: George William Kenneth Cavill, Cyril Maxwell Martin, Andrew David Thomas and Colin Lachlan Adamson.

Popular Science Lecture.—It was announced that the first Popular Science Lecture for 1944 would be given by A. N. Colefax, B.Sc., on Thursday, 15th June, at 8 p.m., the title being "Man and Heredity".

Correspondence.—A letter was received from Dr. J. Pearson, Honorary Secretary of the Royal Society of Tasmania, advising that a replica of the medal which was struck on the occasion of the centenary of the Royal Society of Tasmania was being forwarded to the Royal Society of N.S.W.

The medal had arrived safely, and was on view at the meeting.

Library.—The following donations were received: 85 parts of periodicals and one whole volume.

Lecturettes.—The following lecturettes were given, and were illustrated by lantern slides and special apparatus:

"Physical Aspects of Vision", by R. G. Giovanelli, M.Sc.

"Some Aspects of Physiological Black-out in Aviation", by Professor F. S. Cotton, D.Sc.

July 5th, 1944.

The six hundred and fifteenth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. G. D. Osborne, was in the chair. Thirty members and two visitors were present. The minutes of the previous meeting were read and confirmed.

The death was announced of the following member: Sir Thomas Ranken Lyle, an honorary member since 1931.

Popular Science Lecture.—It was announced that the second Popular Science Lecture for 1944 would be given by J. A. Dulhunty, B.Sc., on Thursday, 20th July, at 8 p.m., the title being "Fuels in the Service of Man".

Library.—The following donations were received: 167 parts of periodicals and nine whole volumes.

The following papers were read:

"Notes on the Nomenclature and Taxonomy of Certain Species of *Melaleuca*", by Edwin Cheel.

"The Chemistry of Bivalent and Trivalent Rhodium. Part IV. Complexes with Diethyl Sulphide", by F. P. Dwyer, M.Sc., and R. S. Nyholm, M.Sc.

Lecturette.—Mr. H. H. Thorne gave a lecturette, entitled "Approximations".

Exhibit.—Dr. A. Bolliger showed an exhibit showing the fluorescence of animal skins, with particular reference to *Trichosurus vulpecula*.

August 2nd, 1944.

The six hundred and sixteenth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. G. D. Osborne, was in the chair. One hundred and twelve members and visitors were present. The minutes of the previous meeting were read and confirmed.

The certificate of one candidate for admission as an ordinary member of the Society was read for the first time.

Popular Science Lecture.—It was announced that the third Popular Science Lecture for 1944 would be given by F. P. J. Dwyer, M.Sc., on Thursday, 17th August, at 8 p.m., the title being "Man and Metals".

Liversidge Lectures.—It was announced that the Liversidge Lectures for 1944 would be given by Dr. F. P. Bowden on August 31st and September 1st, and would be entitled "The Physics of Rubbing Surfaces", Parts I and II.

Library.—The following donations were received: 67 parts of periodicals and one whole volume.

The following papers were read by title only:

"Bessel's Formula in Relation to the Calculation of the Probable Error from a Small Number of Observations", by R. C. L. Bosworth, M.Sc., D.Sc., Ph.D.

"The Light Absorption and Magnetic Properties of Nickel Complexes", by H. A. McKenzie, B.Sc., D. P. Mellor, M.Sc., the late J. E. Mills, M.Sc., Ph.D., and L. Short, B.Sc.

Symposium.—A Symposium was held on "Trace Elements Essential to Life".

The President, Dr. G. D. Osborne, opened the Symposium, and referred to trace elements in minerals, which eventually found their way into soils.

Dr. E. G. Hallsowth spoke on "Trace Elements in the Soil".

Professor E. Ashby's subject was "Trace Elements in Plants", and Dr. J. L. Still spoke on "Trace Elements in Biochemistry".

The following took part in the discussion: Professor R. D. Watt, Drs. A. Albert, F. Lions, R. Breyer, Messrs. F. P. J. Dwyer and D. P. Mellor.

September 6th, 1944.

The six hundred and seventeenth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, 157 Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. G. D. Osborne, was in the chair. Thirty-eight members and twelve visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of two candidates for admission as ordinary members of the Society were read for the first time.

The certificate of one member for admission as an ordinary member of the Society was read for the second time. The following person was duly elected an ordinary member of the Society: Hugh Albert McKenzie.

Liversidge Lectures.—It was announced that, owing to the indisposition of Dr. Bowden, the Liversidge Lectures had been postponed for a few weeks.

Popular Science Lecture.—It was announced that the fourth Popular Science Lecture would be given by Rev. Father D. J. K. O'Connell, S.J., M.Sc., F.R.A.S., on Thursday, 21st September, at 8 p.m., and would be entitled "Man and the Expanding Universe".

Library.—The following donations were received: 104 parts of periodicals and 10 whole volumes.

The following papers were read:

"Review of Analyses of Some Australian Fleece Wools", by M. Lipson, B.Sc., A.A.C.I., and Una A. F. Black, B.Sc.

"The Bauxites of New South Wales. Their Distribution, Composition and Probable Origin", by F. N. Hanlon, B.Sc., Dip.Ed.

"The Determination of Calcite and Aragonite in Invertebrate Shells", by D. M. Bray. (Communicated by F. N. Hanlon, B.Sc.)

"Quaternary Arsonium Salts and their Metallic Co-ordination Compounds. Part I. Bismuth", by F. P. Dwyer, M.Sc., N. A. Gibson, B.Sc., and R. S. Nyholm, M.Sc.

Lecture.—A lecture entitled "The Evolution of Surveying Instruments" was given by Dr. R. L. Aston. The lecture was illustrated by lantern slides and many instruments shown by Dr. Aston to illustrate the evolution of surveying instruments.

Exhibit.—An exhibit was made by Mr. D. P. Mellor of "A Powerful Permanent Magnet in Alnico".

October 4th, 1944.

The six hundred and eighteenth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, 157 Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. G. D. Osborne, was in the chair. Forty members and ten visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of three candidates for admission as ordinary members of the Society were read for the first time.

The certificates of two candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: William Hamilton Watkins and Harry Warner.

Liversidge Lectures.—It was announced that the Liversidge Lectures would be given by Dr. F. P. Bowden on Tuesday and Wednesday, 17th and 18th October, 1944.

Popular Science Lecture.—It was announced that the fifth Popular Science Lecture would be given by F. R. Morrison, A.A.C.I., F.C.S., on Thursday, 19th October, at 8 p.m., the title being "My Lady's Perfume".

Library.—The following donations were received: 180 parts of periodicals and five whole volumes.

The following paper was read:

"The Sternal Integument of *Trichosurus vulpecula*", by A. Bolliger and Margaret H. Hardy.

The following papers were read by title only:

"Studies in the Phenanthridine Series", Parts I-VIII, by E. Ritchie, M.Sc.

Film.—A sound colour film, "Crystals go to War", was shown.

Lecturette.—A lecturette entitled "Some Aspects of Settlement in the Ord River District, North-West Australia", was given by Mr. W. H. Maze.

November 1st, 1944.

The six hundred and nineteenth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. G. D. Osborne, was in the chair. Twenty-seven members were present. The minutes of the previous meeting were read and confirmed.

The death was announced of the following member: Dr. Charles Anderson, a member since 1905.

The certificates of three candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: John Charles Erhart, James Alan Friend and John Bryan Willis.

Exhibition of Photographs.—It was announced that an Exhibition of Photographs of Scientific Interest and a President's "At Home" would be held on Saturday, 25th November, 1944, from 10 a.m. to 12.15 p.m., at the Small Art Gallery, David Jones.

Library.—The following donations were received: 63 parts of periodicals.

The following paper was read by title only:

"Thermal Conductivity from Measurements of Convection", by R. C. L. Bosworth, D.Sc., F.A.C.I.

The following papers were read:

"Quaternary Arsonium Salts and their Metallic Coordination Compounds. Part II. Cadmium", by F. P. Dwyer, M.Sc., N. A. Gibson, B.Sc., and R. S. Nyholm, M.Sc.

"Complexes of Ferric Chloride with Tertiary Arsines", by R. S. Nyholm, M.Sc.

"The Response of Sternal Integument of *Trichosurus vulpecula* to Castration and to Sex Hormones", by A. Bolliger, Ph.D.

Exhibit.—An exhibit was shown by Mr. D. P. Mellor: "The Streaming Double Refraction of Tobacco Mosaic Virus".

Lecturette.—A lecturette on "The Chemical Attack of Tuberculosis" was given by Dr. F. Lions.

December 6th, 1944.

The six hundred and twentieth General Monthly Meeting of the Royal Society of New South Wales, held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. G. D. Osborne, was in the chair. Forty members and five visitors were present. The minutes of the previous meeting were read and confirmed.

The certificates of three candidates for admission as ordinary members of the Society were read for the first time.

Library.—The following donations were received: 90 parts of periodicals and four whole volumes.

The following papers were read by title only:

"A Polarographic Study of the Isomeric Chromium Sulphate", by J. B. Willis, B.Sc.

"The Vibrations of Square Molecules. Part II. The Vibration Frequencies of Planar AB_3C_2 (trans) Molecules", by Allan Maccoll, M.Sc.

"Some Interference Effects with Mica", by O. U. Vonwiller, F.Inst.P.

"A Note on the Magnetic Behaviour of Verdohæmochromogen", by D. P. Craig, M.Sc., and D. P. Mellor, M.Sc.

The following papers were read:

"The Chemistry of Bivalent and Trivalent Iridium. Part II. The Standard Oxidation Reduction Potential for the Chloriridite-Chloriridate System in Hydrochloric Acid Solution", by F. P. Dwyer, M.Sc., H. A. McKenzie, B.Sc., and R. S. Nyholm, M.Sc.

"The Chemistry of Bivalent and Trivalent Rhodium. Part VIII. Rhodic and Rhodous Complexes with Dimethylglyoxime", by F. P. Dwyer, M.Sc., and R. S. Nyholm, M.Sc.

Lecturettes.—Two short addresses on "Some Post-War Problems of New Guinea", were given by Brig.-Gen. Sir Walter McNicoll, K.B.E., C.B., D.S.O., C.M.G., V.D., and Professor A. P. Elkin, M.A., Ph.D.

Walter Burfitt Prize.—It was announced that the Walter Burfitt Prize for 1944 had been awarded to Dr. Hereward Leighton Kesteven, D.Sc., M.D., of Sydney, for his outstanding published work in related fields of osteology, embryology and anatomy of vertebrates.

A. B. WALKOM, President.

ABSTRACT OF PROCEEDINGS
OF THE SECTION OF
GEOLOGY

Chairman : Mr. T. Hodge Smith.

Honorary Secretary : Mr. J. A. Dulhunty.

Seven meetings were held during the year 1944, the average attendance being thirteen members and five visitors.

Meetings.

April 21st.—Annual Meeting. Election of Office-bearers for 1944 : Chairman, Mr. T. Hodge Smith, and Honorary Secretary, Mr. J. A. Dulhunty.

Business : Address by Mr. H. F. Whitworth, " The Commercial Utilization of Rock-Forming Minerals ".

May 19th.—Exhibits and Notes : By Mr. H. O. Fletcher : Aulosteges from Little Gorge Creek, Queensland. By Mr. H. F. Whitworth : An electro magnet for the separation of iron-bearing minerals. By Miss F. M. Quodling : Illustrated note on X-ray methods of locating axes in quartz. By Dr. I. A. Brown : Fossil wood (*Pittus Sussmilchi*) from Babbonboon. By Mr. J. Lambeth : Refractory material consisting of Mullite. By Dr. W. R. Browne : Two types of tributary creeks of the Warragamba River. By Dr. C. A. Anderson : The silicification of wood. By Mr. J. A. Dulhunty : Recent peats from Kosciuszko district.

June 16th.—Address by Dr. G. D. Osborne, " Clay Mineralogy ".

July 21st.—(i) Address by Miss F. M. Quodling, " Fluorescence in Minerals ". (ii) Address by Mr. T. Hodge Smith, " Use of the Ultra-Violet Lamp in Prospecting ". (iii) Address by Dr. G. A. Joplin, " The Origin of Certain Ordovician Gneisses ".

September 15th.—Discussion of Dr. A. B. Walkom's Presidential Address entitled " The Succession of Carboniferous and Permian Floras in Australia ", delivered to the Linnean Society of N.S.W., 1944. Exhibit by Mrs. Sherard : Coloured sketch of ammonite from Tibooburra, and silicified wood from Milparinka.

October 20th.—Address by Mr. C. A. Sussmilch, " Tertiary Volcanic Rocks of Western Australia ". Exhibit by Mr. C. A. Sussmilch : Charts showing submarine topography along west coast of North America.

November 17th.—The death of Dr. C. A. Anderson was announced, with regret. Address by C. Mulholland, " Geological Problems Related to the Southern Intake of the Great Artesian Basin ".

INDEX.

A

	Page.
Abstract of Proceedings	xxi
Section of Geology	xxxi
Analyses of Australian Fleece Wools, Review of	84
Annual Report and Balance Sheet ..	xxii
Authors, Guide to	v
Awards of—	
Clarke Memorial Medal for 1944 ..	xxvii
Walter Burfitt Prize for 1944.. ..	xxx

B

Balance Sheet	xxii
Bauxites of New South Wales, Their Distribution, Composition and Prob- able Origin	94
Bequest, Form of	v
Bessel's Formula in Relation to the Calculation of the Probable Error from a Small Number of Observations ..	81
Bismuth, Quaternary Arsonium Salts and their Metal Co-ordination Com- pounds	118
Black, Una A. F.—	
Review of Analyses of Some Australian Fleece Wools	84
Bolliger, A.—	
The Sternal Integument of <i>Trichosurus vulpecula</i>	122
The Response of the Sternal Integu- ment of <i>Trichosurus vulpecula</i> to Castration and to Sex Hormones ..	234
Bosworth, R. C. L.—	
Bessel's Formula in Relation to the Calculation of the Probable Error from a Small Number of Observa- tions	81
Thermal Conductivity from Measure- ments of Convection	220
Bowden, F. P.—	
Liversidge Lecture—The Physics of Rubbing Surfaces	187
Bray, D. M.—	
The Determination of Calcite and Aragonite in Invertebrate Shells ..	113
Bryan, W. H.—	
Clarke Memorial Lecture—The Re- lationship of the Australian Con- tinent to the Pacific Ocean—Now and in the Past	42

C

	Page.
Cheel, E.—	
Notes on the Nomenclature and Taxonomy of Certain Species of <i>Melaleuca</i>	63
Chemistry of Bivalent and Trivalent Rhodium—	
Part VII. Complexes with Diethyl Sulphide	67
Part VIII. Rhodic and Rhodous Complexes with Dimethylglyoxime ..	266
Chemistry of Bivalent and Trivalent Iridium. Part II. The Standard Oxidation Reduction Potential of the Chloriridite-Chloriridate System in Hydrochloric Acid	260
Clarke Memorial Lecture—	
The Relationship of the Australian Continent to the Pacific Ocean— Now and in the Past	42
Clarke Memorial Medal	xxv
Complexes of Ferric Chloride with Tertiary Arsines	229
Craig, D. P.—See Mellor, D. P. ..	25, 258
Crespin, Irene—	
Some Lower Cretaceous Foraminifera from Boreas in the Great Artesian Basin, Northern New South Wales..	17

D

Determination of Calcite and Aragonite in Invertebrate Shells	113
Dwyer, F. P. J., and Nyholm, R. S.—	
The Chemistry of Bivalent and Tri- valent Rhodium—	
Part VII	67
Part VIII	266
Quaternary Arsonium Salts and their Metal Co-ordination Compounds—	
Part I. Bismuth	118
Part II. Cadmium	226
The Chemistry of Bivalent and Tri- valent Iridium. Part II	260

E

Exhibits	xxv
Extension of Maxwell's Equations ..	14

F

Foulkes, P.—	
Extension of Maxwell's Equations ..	14

G	Page.
Geomorphology of the Central Eastern Area of New South Wales. Parts I and II	28
Gibson, N. A.—See Dwyer, F. P. J. ..	118
Government Grant	xxv
Guide to Authors	v

H	
Hanlon, F. H.— The Bauxites of New South Wales. Their Distribution, Composition and Probable Origin	94
Hardy, Margaret H.—See Bolliger, A. . .	122

I	
Iridium, The Chemistry of Bivalent and Trivalent. Part II. The Standard Oxidation Reduction Potential of the Chloriridite-Chloriridate System in Hydrochloric Acid	260
Isomeric Chromium Sulphates, A Polarographic Study of	239

L	
Landform Analysis, Some Methods of. . .	28
Landform Analysis of the Orange District	28
Lecturettes	xxvii
Light Absorption and Magnetic Properties of Nickel Complexes ..	70
Lipson, M.— Review of Analyses of Some Australian Fleeced Wools	84
List of Members	ix

M	
Maccoll, A.— The Vibrations of Square Molecules. Part II. The Vibration Frequencies of Planar AB ₃ C ₂ (Trans) Molecules	246
Maxwell's Equations, Extensions of ..	14
Maze, W. H.— The Geomorphology of the Central Eastern Area of New South Wales. Parts I and II	28
Mckenzie, A. H.— See Mellor, D. P.	70
See Dwyer, F. P. J.	260
Melaleuca, Notes on the Nomenclature and Taxonomy of Certain Species of. .	63
Mellor, D. P.— A Note on the Role of the Nitrosyl Group in Metal Complexes. . .	25
The Light Absorption and Magnetic Properties of Nickel Complexes ..	70
A Note on the Magnetic Behaviour of Verdohæmochromogen	258

Page.	
Members, List of	ix
Metal Complexes, Light Absorption and Magnetic Properties of	70
Mica, Some Interference Effects with ..	252
Mills, J. E.—See Mellor, D. P.	70

N	
Nitrosyl Group—A Note on the Role of, in Metal Complexes	25
Note on the Role of the Nitrosyl Group in Metal Complexes	25
Note on the Magnetic Behaviour of Verdohæmochromogen	258
Notes on the Nomenclature and Taxonomy of Certain Species of Melaleuca	63
Nyholm, R. S.—See Dwyer, F. P. J. . . .	67, 118, 260, 266
Complexes of Ferric Chloride with Tertiary Arsines	229

O	
Obituaries	2
Officers	vii

P	
Pacific Ocean, Relationship of the Australian Continent to—Now and in the Past	42
Phenanthridine Series, Studies in— Part I. The Cyclisation of 2-Formamido-Diphenyls	134
Part II. The Cyclisation of Some 4'-Bromo and 4'-Dimethylamino Acyl-2-Aminodiphenyls	141
Part III. The Influence of the Acyl Group in the Morgan-Wells Reaction and the Mechanism of the Reaction	147
Part IV. 1:10-Dimethyl Phenanthridines	159
Part V. Phenanthridine-6-Aldehyde and Related Compounds	164
Part VI. A Synthesis of 3-Methyl Phenanthridine	169
Part VII. A Synthesis of Benzo(c)-phenanthridine	173
Part VIII. 3:8-Diamino-Phenanthridine and Related Substances ..	177
Physics of Rubbing Surfaces, The ..	187
Polarographic Study of the Isomeric Chromium Sulphates, A	239
Presidential Address. A. B. Walkom, D.Sc.	1

Q	
Quaternary Arsonium Salts and the Metal Co-ordination Compounds— Part I. Bismuth	118
Part II. Cadmium	226

R	Page.
Report of Council, 1943-44 ..	xxiv
Response of the Sternal Integument of <i>Trichosurus vulpecula</i> to Castration and to Sex Hormones, The ..	234
Revenue Account ..	xxiv
Review of Analyses of Some Australian Fleece Wools ..	84
Rhodium, The Chemistry of Bivalent and Trivalent—	
Part VII. Complexes with Diethyl Sulphide ..	67
Part VIII. Rhodic and Rhodous Complexes with Dimethylglyoxime ..	266
Ritchie, E.—	
Phenanthridine Series, Studies in—	
Part I. The Cyclisation of 2-Formamido-Diphenyls ..	134
Part II. The Cyclisation of Some 4'-Bromo and 4'-Dimethylamino Acyl-2-Aminodiphenyls ..	141
Part III. The Influence of the Acyl Group in the Morgan-Wells Reaction and the Mechanism of the Reaction ..	147
Part IV. 1:10-Dimethyl Phenanthridines ..	159
Part V. Phenanthridine-6-Aldehyde and Related Compounds ..	164
Part VI. A Synthesis of 3-Methyl Phenanthridine ..	169
Part VII. A Synthesis of Benzo(c)-phenanthridine ..	173
Part VIII. 3:8-Diamino-Phenanthridine and Related Substances ..	177
Rubbing Surfaces, The Physics of ..	187

S

Short, L. N.—See Mellor, D. P. ..	70
Some Interference Effects with Mica ..	252
Some Lower Cretaceous Foraminifera from Bores in the Great Artesian Basin, Northern New South Wales ..	17
Square Molecules, The Vibrations of.	
Part II. The Vibration Frequencies of Planar AB ₂ C ₂ (Trans) Molecules ..	246
Sternal Integument of <i>Trichosurus vulpecula</i> ..	122

	Page.
Studies in the Phenanthridine Series—	
Part I. The Cyclisation of 2-Formamido-Diphenyls	134
Part II. The Cyclisation of Some 4'-Bromo and 4'-Dimethylamino Acyl-2-Aminodiphenyls	141
Part III. The Influence of the Acyl Group in the Morgan-Wells Reaction and the Mechanism of the Reaction	147
Part IV. 1:10-Dimethyl Phenanthridines	159
Part V. Phenanthridine-6-Aldehyde and Related Compounds	164
Part VI. A Synthesis of 3-Methyl Phenanthridine	169
Part VII. A Synthesis of Benzo(c)-phenanthridine	173
Part VIII. 3:8-Diamino-Phenanthridine and Related Substances ..	177
Surfaces, The Physics of Rubbing ..	187
Symposium on Trace Elements ..	xxix

T

Tertiary Arsines, Complexes of Ferric Chloride with ..	229
Thermal Conductivity from Measurements of Convection ..	220

V

Verdohæmochromogen, A Note on the Magnetic Behaviour of ..	258
Vibrations of Square Molecules. Part II. The Vibration Frequencies of Planar AB ₂ C ₂ (Trans) Molecules ..	246
Vonwiller, O. U.—	
Some Interference Effects with Mica ..	252

W

Walter Burfitt Prize ..	xx
Willis, J. B.—	
A Polarographic Study of the Isomeric Chromium Sulphates ..	239

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